EFFICIENT NEAR-INFRARED AND ULTRAVIOLET ORGANIC LIGHT EMITTING DEVICES

By

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To my mom
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LIST OF ABBREVIATIONS

AFM: Atomic force microscopy
Ag: Silver
Al: Aluminum
Alq3: Tris(8-hydroxyquinoline) aluminum
AMOLED: Active-matrix organic light-emitting device
BCP: Bathocuproine
BEDOT-TQMe2: 4,9-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-6,7-dimethyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline
BEDOT-BBT: 4,8-bis(2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole
BOLED: Bottom-emitting OLED
BPhen: Bathophenanthroline
CB: Conduction band
CBP: 4,4’-bis(carbazol-9-yl)biphenyl
CCD: Charge coupled device
CCT: Correlated color temperature
CIE: Commission Internationale de L’Eclairage
CRI: Color rendering index
CRT: Cathode ray tube
Cs: Cesium
CT: Charge transfer
CV: Cyclic voltammetry
DAD: Donor-acceptor-donor
DCM: Dichloromethane
DPV: Differential pulse voltammetry
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<td>EBL</td>
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<td>EIL</td>
<td>Electron injection layer</td>
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<td>EL</td>
<td>Electroluminescence</td>
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<td>EM</td>
<td>Electromagnetic</td>
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<td>EML</td>
<td>Emissive layer</td>
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<td>HBL</td>
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<td>MLCT</td>
<td>Metal-ligand charge transfer</td>
</tr>
<tr>
<td>m-MTDATA</td>
<td>4,4',4''-tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbital</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>$\alpha$-NPD</td>
<td>Bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light-emitting device</td>
</tr>
<tr>
<td>OMBD</td>
<td>Organic molecular beam deposition</td>
</tr>
<tr>
<td>Os</td>
<td>Osmium</td>
</tr>
<tr>
<td>OVJP</td>
<td>Organic vapor jet printing</td>
</tr>
<tr>
<td>OVPD</td>
<td>Organic vapor phase deposition</td>
</tr>
<tr>
<td>OXD-7</td>
<td>1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene</td>
</tr>
<tr>
<td>PBD</td>
<td>2-(4-tert-Butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole</td>
</tr>
<tr>
<td>PDP</td>
<td>Plasma display panel</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PHOLED</td>
<td>Phosphorescent organic light-emitting device</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLED</td>
<td>Polymer-based OLED</td>
</tr>
<tr>
<td>PLQY</td>
<td>Photoluminescence quantum yield</td>
</tr>
<tr>
<td>PQIr</td>
<td>Bis(2-phenylquinoline)(acetylacetonate)iridium(III)</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrenesulfonate)</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>Pt-Ar₄TAP</td>
<td>Platinum (II) tetraaryl-tetraanthroporphyrin</td>
</tr>
<tr>
<td>Pt-Ar₂TBP</td>
<td>Platinum (II) diaryl-tetrabenzo-porphyrin</td>
</tr>
<tr>
<td>Pt-Ar₄TBP</td>
<td>Platinum (II) tetraaryl-tetrabenzo-porphyrin</td>
</tr>
<tr>
<td>Pt-DPTBP</td>
<td>Platinum (II) diphenyl-tetrabenzo-porphyrin</td>
</tr>
<tr>
<td>Pt-TBPs</td>
<td>Platinum (II) tetrabenzo-porphyrins</td>
</tr>
<tr>
<td>Pt-TPTBP</td>
<td>Platinum (II) tetraphenyl-tetrabenzo-porphyrin</td>
</tr>
<tr>
<td>Pt-TPTNP</td>
<td>Platinum (II) tetraphenyl-tetrannaphto-porphyrin</td>
</tr>
<tr>
<td>PVK</td>
<td>Poly(9-vinylcarbazole)</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal monitor</td>
</tr>
</tbody>
</table>
RPM  Revolutions per minute
Ru   Ruthenium
SF   Sensitized fluorescence
SMOLED Small-molecule based OLED
SSL  Solid-state-lighting
TAPC 1,1-bis-(di-4-tolylaminophenyl)cyclohexane
TAZ 3-(4-biphenylyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole
TBAPF$_6$ Tetrabutylammonium hexafluorophosphate
TcTa 4,4',4"-tris(carbazol-9-yl)triphenylamine
TIR Total internal reflection
TOLED Top-emitting OLED
TPBi 2,2',2"-(1,3,5-benzenetriyl)-tris(1-phenyl-1-H-benzimidazole)
UGH2 $p$-bis(triphenylsilyly)benzene
UV Ultra-Violet
VB Valence band
VDW Van der Waals
VTE Vacuum thermal evaporation
WOLED White organic light-emitting device
2-AP 2-Aminopurine
3TPYMB Tris[3-(3-pyridyl)mesityl]borane
$A_i$ Normalized amplitude of $i$th decay
$\alpha$ Conversion factor
$E_{ex}$ Exciton binding energy
$E_F$ Fermi level
$E_{opt}$ Optical band gap
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{tr}$</td>
<td>Transport band gap</td>
</tr>
<tr>
<td>$f$</td>
<td>Geometric factor</td>
</tr>
<tr>
<td>$G(\lambda)$</td>
<td>Photopic response</td>
</tr>
<tr>
<td>$G'(\lambda)$</td>
<td>Scotopic response</td>
</tr>
<tr>
<td>$I_{det}$</td>
<td>Photocurrent</td>
</tr>
<tr>
<td>$I_D$</td>
<td>Device current</td>
</tr>
<tr>
<td>$J_D$</td>
<td>Device current density</td>
</tr>
<tr>
<td>$k_{nr}$</td>
<td>Non-radiative decay rate constant</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Radiative decay rate constant</td>
</tr>
<tr>
<td>$k$</td>
<td>Total decay rate constant</td>
</tr>
<tr>
<td>$L$</td>
<td>Luminance</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Solid angle</td>
</tr>
<tr>
<td>$\phi_{em}$</td>
<td>PL quantum yield</td>
</tr>
<tr>
<td>$R$</td>
<td>Radiant emittance</td>
</tr>
<tr>
<td>$R_v$</td>
<td>Radiance</td>
</tr>
<tr>
<td>$S_0$</td>
<td>Ground state</td>
</tr>
<tr>
<td>$S$</td>
<td>Singlet</td>
</tr>
<tr>
<td>$S(\lambda)$</td>
<td>Spectrum</td>
</tr>
<tr>
<td>$\tau_{EL}$</td>
<td>EL lifetime</td>
</tr>
<tr>
<td>$\tau_{em}$</td>
<td>PL lifetime</td>
</tr>
<tr>
<td>$t_{avg}$</td>
<td>Average EL lifetime</td>
</tr>
<tr>
<td>$t_i$</td>
<td>Time constant of \textit{i}th decay</td>
</tr>
<tr>
<td>$T$</td>
<td>Triplet</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
</tr>
</tbody>
</table>
\( \eta_L \)  
Current efficiency (or luminance efficiency)

\( \eta_{LP} \)  
Luminous power efficiency

\( \eta_P \)  
Power efficiency

\( \eta_{IQE} \)  
Internal quantum efficiency

\( \eta_{EQE} \)  
External quantum efficiency

\( \eta_{out} \)  
Outcoupling efficiency
EFFICIENT NEAR-INFRARED AND ULTRAVIOLET ORGANIC LIGHT EMITTING DEVICES

By

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December 2011

Chair: Jiangeng Xue
Major: Materials Science and Engineering

There has been a growing interest in the development of extreme light sources including near-infrared (near-IR) and ultraviolet (UV) emitting organic light-emitting devices (OLEDs) due to their potential applications. Existing near-IR and UV OLEDs generally have low external quantum efficiencies and limited choice of emitter materials. So, new materials and devices need to be developed to achieve OLEDs with tunable emission and high efficiency in near-IR and UV ranges.

In the first part of this dissertation, we achieve very nice coverage of the near-IR emission range from 700 nm to over 1000 nm, by using different novel near-IR emitting materials. Fluorescent near-IR OLEDs based on two donor-acceptor-donor oligomers, BEDOT-TQMe₂ and BEDOT-BBT, are first demonstrated with maximum external quantum efficiency (EQE) up to 1.6% and emission peak wavelengths over 800 nm. The efficiencies of these fluorescent OLEDs are further increased by two to three times by using sensitized fluorescence structure to funnel the triplet excitons formed on the host molecules to the fluorescent emitters, which are not utilized in fluorescent devices. Even higher efficiencies and longer emission wavelengths are achieved by phosphorescent near-IR OLEDs based on extended conjugation Platinum (II)
porphyrins, with record high EQE of 9.2%. Furthermore, we do realize that the PL efficiencies in solution do not necessarily carry over to the EL efficiencies of devices.

In the second part, towards the short wavelength end of the visible light range, a blue-violet emitting device has been constructed featuring a highly fluorescent donor-acceptor purine in the emissive layer, with a maximum EQE of 3.1% and peak emission at 430 nm. With different donor groups connected to the purine heterocycle ring, another purine derivative with further blue-shifted emission is also employed for UV emitting OLEDs, achieving a maximum EQE of 1.5% and emission peak below 400 nm, at wavelength of 393 nm. We realize that, due to the high energy band gap of UV emitting molecules, it is very important to appropriately align the energy levels of different layers in multilayer UV OLEDs to efficiently extract the desired light emission.
CHAPTER 1
INTRODUCTION TO ORGANIC LIGHT-EMITTING DEVICES

1.1 Lighting-Emitting Devices (LEDs)

There has been an enormous increase in the global demand for energy in recent years as a result of industrial development and population growth. Nowadays, 85% of the world’s energy supply is still from the non-renewable energy including oil, coal and natural gas, which will be used up in a very close future due to huge demand of energy.\(^{1-6}\) To balance the energy demand and supply, it is imperative to develop new sources of energy such as wind, solar and nuclear energy. On the other hand, the introduction of efficient electronic devices is also necessary to reduce the consumption of electric power, and therefore mitigate the energy crisis. Currently, research into high efficiency and energy saving solutions is widely studied and gained top priority.

Among all the energy consumed, lighting in buildings in the United States consumes \(~765\) TeraWatt-hours (TWh) of electricity a year, which accounts for approximately 22% of the total electricity, with 40% of that amount consumed by inefficient incandescent lamps.\(^7\) The incandescent light usually has the power conversion efficiency as low as 5%, which means 95% of the supplied energy is wasted as heat. Another common light source, fluorescent tube, has better power conversion efficiency of 20%. However, fluorescent tubes contain hazardous mercury which is not environmentally friendly.\(^8\) Given these figures, it is easy to see that if the efficiency of lighting can be increased to more than 20%, it would bring tremendous energy savings.

One alternative solution is to use the solid state lighting. Rather than electrical filaments or plasma, solid state lighting (SSL) uses semiconductor materials based light emitting devices (LEDs) as sources of illumination with high efficiency. Conventional
LEDs are made of inorganic semiconductors, mostly group III-nitride, which have direct band gaps and can convert the electric energy directly into the light emission with less energy loss. Although almost 100% internal quantum efficiency could be achieved by using inorganic LEDs, there are still a few issues such as high cost of materials and processing, low color rendering index (CRI) for white light sources, and difficulty for device scalability. Nevertheless, the inorganic LEDs market has been expanded to more and more fields in the last few years. Figure 1-1 shows several examples of white LEDs for application of lighting.

Figure 1-1. (color) Examples of white LEDs for lighting. A) A white LED from Cree. B) Recessed downlight. C) Audi LED headlight. D) Portable desk/task lighting.

As the name indicates, organic light-emitting devices (OLEDs), a new generation of LEDs, use the organic materials including polymers as the active electroluminescent materials in response of the input electric power. Since the OLEDs were first demonstrated by Tang and Vanslyke in 1987 at Eastman Kodak, extensive research has been conducted in academia and industry to achieve comparable high efficiency
and practical OLEDs. Figure 1-2 schematically compares the performance and progress of different light sources including inorganic and organic LEDs.\textsuperscript{12} It clearly shows that the performance of OLEDs has developed very fast and now has surpassed the conventional low efficiency incandescent light and can be competitive with the LEDs and fluorescent light. Other than that, OLEDs have many advantages over the other light sources, such as low cost, low temperature processing, compatible with flexible and large area substrates, tunable material properties via structure modification. Details will be discussed in the following section.

Figure 1-2. (color) Performance and current progress of several light sources including inorganic and organic LEDs.\textsuperscript{12} The performance is presented by power efficiency (lm/W).

1.2 Advantages of Organic Light-Emitting Devices

There are many advantages for organic semiconductors used for organic light emitting devices. To date, about two million organic compounds have been made and this constitutes nearly 90\% of all known materials in the world. So, organic materials provide a huge amount of choices for specific device fabrication requirements. And their
electronic and optical properties can be easily tailored by chemical structure modification. For example, the emission spectra of the phosphorescent cyclometalated platinum complexes developed for organic light emitting devices can be tuned throughout the visible spectrum by simply changing the functional cyclometalating ligand conjugation,\textsuperscript{13} as shown in Figure 1-3. Most organic materials are inexpensive, although currently the cost for some materials may be substantial due to the low yield of chemistry synthesis or difficulties in the purification.

![Figure 1-3. (color) Commission Internationale de L'Eclairage (CIE) color coordinates of various phosphorescent cyclometalate platinum complexes.\textsuperscript{13}](image)

Another advantage of organic materials is the compatibility with low cost and large-area manufacturing processes. Vacuum thermal evaporation (VTE)\textsuperscript{14} or organic vapor phase deposition (OVPD)\textsuperscript{15,16} are usually used to deposit small molecular organic thin films. Polymer semiconductors can be processed from solution by casting, spin-coating and ink-jet printing.\textsuperscript{17,22} These processes only require at or near room
temperature processing, which is significantly lower than required for most inorganic materials. Some of these deposition techniques are compatible with large-area, flexible\textsuperscript{23} and roll-to-roll processing,\textsuperscript{24-30} leading to potentially high-throughput manufacturing of organic electronic devices. Figure 1-4 shows some flexible OLEDs (FOLEDs) applications available in the market.

Figure 1-4. (color) Examples of flexible OLEDs (FOLED) applications: A) 4.5 inch flexible AMOLED display by Samsung Mobile Display (SMD®); B) Flexible OLEDs on garments.

OLED displays also have many merits such as fast response time, wide viewing angle, high contrast, and low power consumption, compared to the main competitor, liquid crystal displays (LCDs).

1.3 Applications of Organic Light-Emitting Devices

There are mainly two applications of OLEDs, especially the white light OLEDs (WOLED). The first is the flat panel display device where OLEDs are considered as the next generation display technique and will competes with the conventional LCDs. The other application is to be used as the next generation solid-stae lighting source to replace the conventional low efficiency incandescent light bulbs and even fluorescent tubes. There are already many commercialized products in the market for both applications of OLEDs.
1.3.1 Flat Panel Display

LCDs have replaced cathode ray tube (CRT) displays in more and more applications and been today’s dominant flat panel display technology, due to its advantages of wide variety of display sizes, energy efficient and environment safe. Compared to LCDs, OLEDs are capable of providing markedly better performance features, including thinner and lighter design, faster response times, wider viewing angles, higher contrast ratios and brighter, more saturated colors. OLEDs can also be more energy efficient than LCDs with operating lifetimes now in the tens of thousands of hours. The fabrication of OLED displays also has the potential to be cost effective with those low-cost and high-throughput manufacturing methods like roll-to-roll processing. There have been many commercialized products in the market, as shown in Figure 1-5.

Figure 1-5. (color) Various OLEDs display applications: A) 11” OLED display (Sony ®); B) 4” active-matrix OLED display for Galaxy S smartphone (Samsung ®); C) 31” OLED TV (LG ®); D) 40” OLED TV (Samsung ®).
The first commercialized 11" OLED display, XEL-1, was released by Sony ® in 2007 as shown in Figure 1-5A, with only 3 mm thick. Nowadays, active-matrix OLED (AMOLED) has been widely used for cell phone screen display. Figure 1-5B shows the world largest flexible AMOLED with a WVGA 800x480 pixel resolution by Samsung ®. Since the relatively small-size of OLED displays have been widely introduced to the market, large-size prototype OLED TVs (31"-40" and above) have been also continuously reported as shown in Figure 1-5C and D. Several companies including DuPont ® and LG ® had stated that they can produce the even larger size OLED TVs up to 50 inch in minutes. Moreover, it is expected that the OLEDs would be more compatible in realizing the 3-D images due to their fast response.

1.3.2 White OLEDs Lighting

The primary requirements for a general illumination light source lie in three aspects: high power efficiency at high brightness, high CRI, and high stability at high brightness. The conventional incandescent lamps are widely used but very inefficient (~15 lm/W). This has generated increased interest in the use of WOLEDs, owing to their potential for significantly improved efficiency and higher CRI over incandescent sources combining with low-cost, high-throughput manufacturability. Currently, the efficiencies of WOLEDs can be achieved by 40-60 lm/W31-33 and this value can be increased to more than 100 lm/W if light outcoupling enhancement techniques are employed. Meanwhile, lifetimes longer than 10,000 hours for WOLED are also demonstrated. In terms of efficiency and stability, WOLED lighting has definitely surpassed the incandescent lamps and can be even competitive with the fluorescent light tubes.

Except for the merits of high efficiency and stability, WOLED is also a surface light emitting source which allows great design freedom in producing new concept lightings.
They can be fabricated on any substrates including the flexible ones and are able to make lighting devices in any shapes and designs. Figure 1-6 shows several existing white OLED lighting products.

Figure 1-6. (color) Examples of OLEDs lighting applications: A) 30 cm lighting panels; B) GE ® 24”x24” light tiles; C) Flexible OLED general lighting by GE ® and Konica Minolta ®.

1.4 High Efficiency Blue and White PHOLEDs

The OLED applications such as flat panel display and solid state lighting require integrating individual pixels of blue (B), green (G), and red (R) emission to realize the white OLEDs. While green-emitting phosphorescent OLEDs (PHOLEDs) with nearly 100% internal quantum efficiency have been demonstrated, improving the efficiency and stability of blue-emitting OLEDs is, however, one of the remaining challenges in OLEDs for full color display and lighting source applications. Blue phosphorescent emitting materials usually have higher triplet excited energy levels as the blue emission goes to shorter wavelengths. So it is much more difficult to effectively confine the
excitons in the blue emitters by using the typical host and charge transporting materials which work well for green and red emitters in OLEDs.

Most of the works on blue OLEDs have been focused on phosphorescent metal-organic complexes such as FIrpic\textsuperscript{36} and FIr6.\textsuperscript{37,38} FIr6 based devices show deep-blue emission,\textsuperscript{37,39} while FIrpic exhibits greenish-blue color, which is not sufficient for practical full color displays and lighting applications.\textsuperscript{40} However, FIr6 has a higher triplet energy (T\textsubscript{1}) of 2.72 eV,\textsuperscript{41} compared to 2.65 eV for FIrpic.\textsuperscript{36} Holmes et al. used a wide-gap material, UGH2 with high triplet energy of 3.5 eV\textsuperscript{41} and inserted an mCP layer (T\textsubscript{1} = 2.9 eV)\textsuperscript{36} between the hole transporting layer and the emissive layer to serve as the efficient electron/exciton blocking layer.\textsuperscript{37} A maximum external quantum efficiency ($\eta_{\text{EQE}}$) of 12\% and power efficiency ($\eta_{\text{P}}$) of 14 lm/W at low luminances were demonstrated by this device structure. The power efficiency can be further improved by employing the $p$-$i$-$n$ dual emissive layer (D-EML) structures. A low turn-on voltage of 3.2 V and a maximum power efficiency of 25 lm/W were achieved.\textsuperscript{42} By carefully choosing the charge transporting layers with high triplet energies to better confine the excitons, maximum $\eta_{\text{EQE}}$ of 20\% and peak $\eta_{\text{P}}$ of 36 lm/W were achieved maintaining CIE coordinates of (0.16, 0.28).\textsuperscript{43} Some existing efficient blue OLEDs are listed in Table 1-1. Nonetheless, alternative materials and device structures are still needed to further enhance the performance of blue OLEDs, in order for display and lighting applications.

Since the first demonstration of white organic light-emitting devices (WOLEDs) by Kido et al.,\textsuperscript{44-47} there have been many different approaches, trying to enhance the device efficiency so that WOLEDs can be used for solid-state lighting and displays to replace the conventional products. These devices have now surpassed incandescent
light bulbs (~15 lm/W) in terms of efficiency and lifetime. Active research has been focused on further improving their device efficiency to beyond that of fluorescent light (60-90 lm/W) and achieving high color rendering indices (CRI). Su et al. has reported high efficiency white PHOLEDs with a peak power efficiency of 44 lm/W using two phosphorescent dopants of a greenish-blue emitter, FIrpic, and a red emitter, PQ2Ir. Due to the limited spectral coverage of the two emitters, this device possessed a low CRI of only 68 in spite of the high efficiency. To improve the spectral coverage of WOLEDs, a blue fluorescent emitter in combination with green and red phosphor dopants has been exploited in the EML with a high CRI of 85, and maximum $\eta_p$ of 22 lm/W. WOLEDs based on all phosphorescent dyes of deep-blue emitter, FIr6, green emitter, Ir(ppy)$_3$, and red emitter, PQIr have also been demonstrated with maximum $\eta_{EQE}$ of 12% and CRI of 80. The efficiencies can be further improved with enhanced charge and exciton confinement in the EML by charge transporting layers as reported by Xue et al., achieving maximum $\eta_{EQE}$ of 19% and peak power efficiency of 40 lm/W. Only recently, Universal Display Corporation (UDC®) has announced all phosphorescent WOLED lighting panels with record high power efficiency of 58 lm/W, CRI of 83, and operating lifetime of 30,000 hours (to 70% of initial luminance). Some recent research progress of efficient WOLEDs is listed in Table 1-1.

Moreover, the planar OLEDs structure will typically suffer from low light extraction efficiency of approximately 20%. The light output from emissive layer in OLEDs will be reduced by absorption losses and wave guiding within the device and its substrate due to total internal reflection (TIR) at multiple interfaces. Numerous works have been reported to further improve the light extraction efficiencies in OLEDs, and recent
reports from UDC ® show the peak power efficiency higher than 100 lm/W has been demonstrated with incorporation of light outcoupling enhancement techniques, which is already very competitive with the conventional fluorescent light source.

Table 1-1. Recent research progress of blue (B) and white (W) OLEDs. The maximum external quantum (\( \eta_{\text{EQE}} \)) and power (\( \eta_{\text{P}} \)) efficiencies, the CIE \((x, y)\) coordinates, and CRI are shown for comparison.

<table>
<thead>
<tr>
<th>OLED architecture</th>
<th>( \eta_{\text{EQE}} ) (%)</th>
<th>( \eta_{\text{P}} ) (lm/W)</th>
<th>CIE ((x, y))</th>
<th>CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>12%</td>
<td>14 lm/W</td>
<td>(0.16,0.26)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>( p-i-n ) D-EML with FIr6 as blue emitter[^{37}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>17%</td>
<td>25 lm/W</td>
<td>(0.16,0.28)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>( p-i-n ) D-EML with FIr6 as blue emitter[^{37}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>20%</td>
<td>36 lm/W</td>
<td>(0.16,0.28)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>WOLED with 3TPYMB as ( \text{ETL} )^[^{43}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W1</td>
<td>25%</td>
<td>44 lm/W</td>
<td>(0.34,0.40)</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>Fluorescent blue emitter with FIrpic and PQ2Ir[^{32}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W2</td>
<td>11%</td>
<td>22 lm/W</td>
<td>(0.38,0.40)</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Green and red phosphor dopants[^{48}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W3</td>
<td>12%</td>
<td>26 lm/W</td>
<td>(0.43,0.45)</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Phosphorescent triple-doped EML[^{35}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W4</td>
<td>19%</td>
<td>40 lm/W</td>
<td>(0.37,0.40)</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Phosphorescent triple-doped D-EML with ( p-i-n )^[^{31}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W5</td>
<td>All phosphorescent WOLED lighting panel (UDC ®)[^{8}]</td>
<td>-</td>
<td>58 lm/W</td>
<td>83</td>
</tr>
</tbody>
</table>

1.5 Near-Infrared and Ultra-Violet OLEDs

Since the first report of near-infrared (NIR) emission from an organic light-emitting device (OLED) based on a lanthanide complex,\[^{55}\] there has been considerable interest in the development of materials and devices that exhibit wavelength tunable and efficient light emission in the NIR wavelength region. Such work is of interest for a variety of applications in security and defense, telecommunications, and biomedical sectors,\[^{56-63}\] as shown in Figure 1-7. For example, NIR OLEDs could serve as a new class of illuminators for night vision, providing advantages such as light weight, low thermal signature, low power consumption, and compatibility with large area and flexible
substrates. Much of the existing work on NIR OLEDs has focused on the use of lanthanide-containing organometallic complexes based on Yb, Nd, and Er.\textsuperscript{55,56,64-73} The metal phthalocyanines (Pc) with emissions at the near-IR range are also used for the device demonstration.\textsuperscript{74,75} However, because of the inherent low efficiency of emission from these complexes, the most efficient OLEDs based on these materials possess external quantum efficiencies (EQE) less than 0.3%.

Phosphorescent transition metal-organic complexes provide attractive candidates for use in PLEDs and OLEDs due, in part, to their high luminescence quantum yields and nearly 100% internal quantum efficiencies due to their ability to efficiently emit from the spin-orbit mixed triplet states.\textsuperscript{34,35}

![Image of various near-IR light source applications: A) Night vision; B) Heating; C) Thermal bandage healing; D) Telecommunication.]

A recent report of an electrophosphorescent device that used a cyclometalated [(pyrenyl-quinolyl)\textsubscript{2}Ir(acac)] complex as the phosphor gave $\lambda_{max}$ = 720 nm and an EQE of 0.1%.\textsuperscript{76} More specifically, a subclass of phosphorescent metal-organic complexes, metalloporphyrins, has shown intense absorption and emission in the red-to-NIR region.
of the spectrum. There are a number of reports of OLEDs fabricated with PtOEP, PtTPP, or analogues of these compounds as phosphorescent emitters, with emission maxima between 630 and 650 nm. Porphyrin chromophores with fused aromatic moieties at the β-pyrrole positions, for example, tetrabenzoporphyin (TBP), exhibit a bathochromic shift (relative to unsubstituted porphyrin) of the absorption and emission energy, owing to the expansion of the π-electronic system of the porphyrin core. The addition of bulky groups to the meso positions of the porphyrin macrocycles with β-substituted pyrroles leads to the formation of nonplanar porphyrins, and further red-shifts the absorption spectra. Based on these considerations, π-extended Pt-porphyrin complexes such as Pt-tetraphenyltetrabenzoporphyrin (Pt-TPTBP) have been studied for NIR OLEDs with a reported maximum EQE of 8.5% and a peak wavelength of 770 nm. Despite the high efficiencies, there still remains the need for the development of alternative materials and devices that exhibit wavelength tunable and highly efficient emission at \(\lambda > 800\) nm.

Another interest has recently turned to organic systems that emit at the other end of the visible range, the shorter wavelengths - from the deep blue, through the violet, to the ultraviolet regions. Ultraviolet (UV) to deep blue organic light-emitting diodes (OLEDs) have found, or are sought for, applications in biological and chemical sensing, sterilization, high-density information storage devices, and full-color light-emitting displays, as shown in Figure 1-8. Recently, there have been several reports of high efficiency fluorescent blue-to-violet OLEDs with a peak emission wavelength in the range of 400-450 nm that possess maximum EQE values up to 3-4%, although the shorter wavelength emission generally leads to lower device efficiencies.
Despite a number of examples of deep blue to UV emitting OLEDs based on organic fluorescent emitters, including small molecules\textsuperscript{101-108} and polymers,\textsuperscript{99,100,109,110} only a few\textsuperscript{106,108} realize the device emission peak wavelengths below 400 nm, which can be considered as the UV emission, with external quantum efficiencies (EQE) greater than 1%. However, these so-called UV OLEDs still have relatively broad emission peaks, with emission tail extending as far as to the longer wavelength ranges of 450-550 nm.

Figure 1-8. (color) Various ultra-violet light source applications: A) Protein in jellyfish that glowed bright green under UV light (Nobel Prize 2008); B) A collection of mineral samples brilliantly fluorescing at various wavelengths as seen while being irradiated by UV light; C) Blu-ray disc using blue-violet laser to read the information; D) Sterilization of food and tools.

The challenges of fabricating UV OLEDs lie in two parts: one is the molecular design of materials capable of efficient UV emission,\textsuperscript{106} and the other is appropriately designed device structure,\textsuperscript{108,111,112} where both hole and electron carriers are injected into a wide energy band gap UV emitting material and non-UV emissions from longer wavelength emitting materials need to be prevented. So, highly sought are organic materials that can achieve emissive color tunability and provide high efficiency and
brightness in the UV to violet region, and device structures with appropriate energy levels alignment.

1.6 Outline of Dissertation

This dissertation endeavors to deliver the fundamental background of OLEDs as well as material study and device design for high efficiency near-IR and UV OLEDs. First, Chapter 2 will explain the optical, electrical, and physical properties of organic semiconductors. Chapter 3 will help understanding more details about OLEDs from the organic thin film growth to OLED measurements. The important terminologies and definitions for understanding the OLED operation and evaluation will be described in Chapter 3 as well. In Chapter 4 and 5, high efficiency fluorescence and phosphorescence near-IR OLEDs will be demonstrated by employing donor-acceptor-donor oligomers and Platinum (II) porphyrins, respectively. The effect of molecular structure for both types of NIR emitters on the device performance will also be studied. In Chapter 6, efficient blue-violet and violet-UV emitting OLEDs will be demonstrated based on the highly fluorescent donor-acceptor purines. The challenges of fabricating UV OLEDs will be realized and then the effect of energy level alignment in the multilayer devices on acquiring desired device emissions will be investigated. Finally, this dissertation will make conclusions and leave some future topics for further OLEDs especially UV emitting OLEDs as well as for organic photovoltaic (OPV) device research in Chapter 7.
CHAPTER 2
PHYSICS OF ORGANIC SEMICONDUCTORS

2.1 Introduction to Organic Semiconductors

Organic semiconductors differ significantly in their optical, mechanical, and electronic properties from the conventional covalent solid semiconductors such as Si, Ge, II-VI and III-V semiconductors, which have been used as the active materials in electronic and optoelectronic devices. This can be mainly attributed to the different bonding interactions between the constituent atoms or molecules for the organic and conventional semiconductor materials. The majority of organic materials belong to the category of molecular solids, and the intermolecular interaction forces that hold the molecules together is primarily of the van der Waals (VDW) force, which is considerably weaker than that of covalent or ionic bonds in the conventional semiconductors.\textsuperscript{113,114}

Organic semiconductors have a number of advantages over their inorganic counterparts. To date, about two million organic compounds have been made and this constitutes nearly 90% of all known materials in the world. So, organic materials provide a huge amount of choices for a particular application. And their electronic and optical properties can be easily tailored by chemical structure modification.\textsuperscript{13} Most organic materials are inexpensive, although the cost for some materials may be substantial due to the low yield of chemistry synthesis or difficulties in the purification.

Another advantage of organic materials is the compatibility with low cost and large-area manufacturing processes. Vacuum thermal evaporation (VTE)\textsuperscript{14} or organic vapor phase deposition (OVPD)\textsuperscript{15,16} are usually used to deposit small molecular organic thin films. Polymer semiconductors can be processed from solution by casting, spin-coating and ink-jet printing.\textsuperscript{17-22} These processes require at or near room temperature
processing, which is significantly lower than required for most inorganic materials. Some of these deposition techniques are compatible with large-area, flexible and roll-to-roll processing, leading to potentially high-throughput manufacturing of devices. Despite the above advantages, organic semiconductors face some challenges for use in electronic and optoelectronic devices. Due to the weak intermolecular interactions of van der Waals force, organic materials generally have much lower carrier motilities than inorganic materials. The purification of organic materials is also problematic, as no available purification method can achieve organic materials with purities reaching that of, for example, silicon. Finally, most organic materials are susceptible to degradation when exposed to water vapor, oxygen and other contaminations. So, their reliability and stability in electronic and optoelectronic devices are in question.

![Classification of organic semiconductors with increasing structural complexity](image)

**Figure 2-1.** (color) Classification of organic semiconductors with increasing structural complexity. The molecules shown from left to right are: an Al-quinoline complex small molecule (left), a polymer PPV (middle), and a protein complex (right).

Depending on the structural complexity and molecular weight, organic semiconductors can be further divided into three types: small molecules, polymers, and biological molecules, as shown in Figure 2-1. Small molecules usually have molecular weight less than 1000 and have well-defined molecular structures. Polymers...
are long-chain molecules consisting of an undefined number of repeating units. Their molecular weight can be anywhere from a few thousand to a million. The molecules having the highest structural complexity are of biological origin, such as DNA and protein. Small molecules and polymers have been extensively used as the active materials in electronic and optoelectronic devices, while the use of biological molecules in electronic applications has not been clearly demonstrated.

2.2 Electronic Structures of Organic Semiconductors

Figure 2-2 shows several examples of typical organic semiconductors used in electronic and optoelectronic devices. The framework of the organic molecules is usually composed of the carbon atoms connected by different bonds such as single and double bonds. Other atoms, for example, sulfur or nitrogen atoms, sometimes are also incorporated. For the carbon atom, the electronic configuration in the ground state is \(1s^22s^22p^2\), as shown in Figure 2-3, with two paired electrons in \(2s\) orbital and two unpaired electrons in two \(2p\) orbitals.

![Figure 2-2. Examples of several organic semiconductors including small molecules and polymers used in electronic and optoelectronic applications.](image)
Due to the Pauli Exclusion Principle, only the unpaired $2p$ electrons in carbon atom may be shared with other atoms to form covalent bonds. The paired $2s$ orbital, however, may mix or hybridize with one or more $2p$ orbitals, leading to the hybridized orbitals of $sp$, $sp^2$, and $sp^3$, with single electron occupancy in each orbital, as shown in Figure 2-3. The hybridized orbital configurations are more favorable than the ground state for the carbon atoms to form covalent bonds with other atoms, as all four valence electrons are now unpaired and available for bonding.

![Figure 2-3. Electronic configurations of a carbon atom in the ground state and $sp^n$ hybridized states ($n = 1, 2, 3$).](image)

When two carbon atoms are bonded together, the inter-atomic interaction leads to the formation of bonding and anti-bonding molecular orbitals (MOs). Figure 2-4 shows the formation of the molecular orbitals of two adjacent carbon atoms with $sp^2$ hybridization. The $\sigma$ bonding and anti-bonding ($\sigma^*$) MOs can be formed between the two $sp^2$ hybridized orbitals, one from each carbon atoms. Similarly, the remaining two $sp^2$
hybridized orbitals in a carbon atom may form more σ bonding and anti-bonding MOs with s, p, or \( sp^n \) orbitals of other atoms. The π bond and anti-bonding (π *) MOs can be formed between the two \( p_z \) orbitals of the carbon atoms. The σ bonding MO has lower energy than π bonding MO, while the anti-bonding MOs of σ and π bonds exhibit the opposite trend. So the four electrons will occupy the low-lying energy levels first, and a σ bond and a π bond are then formed, as shown in Figure 2-4A. The σ bond is formed with the two \( sp^2 \) hybridized orbitals connected in the head-on geometry, whereas the two \( p_z \) orbitals interact side by side to form the π bond, as illustrated in Figure 2-4B. The strength of the σ bond is higher than that of the π bond, as the overlap between the orbitals for σ bond is more effective.

![Figure 2-4. Molecular orbitals (MOs) of two adjacent carbon atoms with \( sp^2 \) hybridization: A) Formation of σ and π bonding and anti-bonding MOs; B) Schematic illustration of the bonding between the two adjacent carbon atoms.](image)

Furthermore, according to Hund’s rule and the Pauli Exclusion Principle, the π bonding and π * anti-bonding molecular orbitals are the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) for this molecule. Since the lowest excited states of a molecule involve the HOMO and LUMO, the π bonding and π * anti-bonding MOs play an important role in determining various electronic properties of the molecule.
For a molecule containing several atoms, the electronic structure of this molecule can be treated in the same way as the situation of two atoms, although the results may be much more complicated. Figure 2-5A shows a simple example of the electronic structure of benzene (C₆H₆) molecule. All the six carbon atoms have the $sp^2$ hybridization and are connected with alternating single and double bonds. A delocalized super $\pi$ bond is formed by the six $p_z$ orbitals, leading to all six carbon atoms and the bonds between them being equivalent. Hence, rather than using alternating single and double bonds, the structure of benzene with a circle inside the carbon hexagon skeleton, as shown in Figure 2-5A, is usually used to represent the delocalized $\pi$ bond.

Figure 2-5. A) Resonance molecular structure of a benzene molecule (C₆H₆) and the delocalized $\pi$ bond formed by six $p$-orbitals. B) Extended conjugation system.

The extension of the conjugation will lead to a general delocalization of the electrons across all of the adjacent parallel aligned $p$-orbitals of the atoms, which will lower the overall energy of the molecule and enable the charge transport within the
organic molecule, as shown in Figure 2-5B. Additionally, the band gaps of the organic molecules are strongly affected by the degree of conjugation, i.e. more conjugated molecules have smaller band gaps and thereby longer absorption maximum.

### 2.3 Charge Transport

In general, the dynamics of charge carrier motion in solids has two extreme types: one is highly delocalized motion in the form of a Bloch wave, and the other is highly localized as a result of interactions with the local surroundings. Actual systems fall between these two extremes due to the competition between energies associated with the delocalization and localization processes.

![Energy level diagrams](image)

Figure 2-6. Energy level diagrams of a single molecule in gas phase, ionized electron and hole pairs in the solid crystal, and a disordered Gaussian density of states in an amorphous solid. \(^\text{116}\)

Localizing a charge carrier in wave-like motion to form a wave packet requires certain energy. Such a localization energy is a direct result of the uncertainty principle. Narrow bands are formed in organic materials with weak intermolecular interactions. The large density of states in a narrow band leads to a relatively small localization energy, and the tendency towards carrier localization is more pronounced in organic
On the other hand, the interaction between a charge carrier and its electronic and nuclear surroundings causes local polarization, which lowers the total energy of the system, as shown in Figure 2-6. The change in the total energy is called the polarization energy. For the amorphous solids, locally different polarization energies create a Gaussian distributed density of states for transporting sites.

The mobility for delocalized charge carriers is usually high, as they transport in wide energy bands. For strongly localized carriers, they move via stochastically uncorrelated hopping motion from site to site, and the mobility is generally low and is thermally activated. Organic semiconductors usually have several orders of magnitude lower charge transport capabilities, compared to their inorganic counterparts. A strong covalent bond is formed in inorganic semiconductors, creating the delocalized states and leading to the continuous transport energy band, whereas, a weak VDW interaction creates discontinuous localized states in organic semiconductors, resulting to the less efficient charge hopping transport.

2.3.1 Hopping Transport

Most organic thin films are in an amorphous solid state, and the weak VDW interactions throughout the amorphous structure creates discontinuous localized states in the organic molecules, instead of a continuous transporting energy band. So, an intermolecular hopping transport mechanism dominates in the amorphous solid state. The typical charge carrier mobility ($\mu$) of amorphous organic semiconductors is in the range of $10^{-3}$-$10^{-10}$ cm$^2$/V-s. The mobility in amorphous organic semiconductors can be expressed as a function of electric field and temperature:\(^{117}\)

$$
\mu(F,T) \propto \exp\left(\frac{-\Delta E}{kT}\right) \cdot \exp\left(\frac{\beta \sqrt{F}}{kT}\right)
$$
where, $F$ is the electric field, $T$ is the temperature, $\Delta E$ is the activation energy for intermolecular hopping, $k$ is Boltzmann constant, and $\beta$ is a constant.

### 2.3.2 Band Transport

Band transport has been observed in high quality organic molecular crystals such as pentacene, anthracene and naphthalene, with a slightly delocalized transport energy band and room temperature mobility of $\mu_{\text{RT}} \approx 1 \text{ cm}^2/\text{V-s}$.\textsuperscript{114,118,119} The mobility for crystalline organic semiconductor has a temperature dependence:\textsuperscript{120}

$$\mu(T) \propto T^{-n} \quad (n > 1)$$

However, in most cases, the weak intermolecular interactions and the strong polarizability of organic molecules lead to localization of charge carriers in organic materials, and a thermally activated mobility with $\mu_{\text{RT}} < 1 \text{ cm}^2/\text{V-s}$ is obtained.\textsuperscript{114}

### 2.3.3 Transport vs. Optical Band Gaps

Typically for inorganic semiconductors, there is a negligible difference between the optical band gap ($E_{\text{opt}}$) and transport band gap ($E_{\text{tr}}$) due to the small exciton binding energy ($\sim 10$ meV) in delocalized energy states. However, for organic semiconductors, the $E_{\text{opt}}$ and $E_{\text{tr}}$ should be differentiated due to the strong exciton binding energy ($\sim 1$ eV) in the localized organic molecules.\textsuperscript{114} The accurate relationship of $E_{\text{opt}}$ and $E_{\text{tr}}$ for organic semiconductors can be expressed as:

$$E_{\text{opt}} = (E_{\text{gap}} - E_{\rho}) - E_{\text{ex}} = E_{\text{tr}} - E_{\text{ex}}$$

where, $E_{\text{gap}}$ is the energy level difference between the HOMO and LUMO in a single molecule, $E_{\rho}$ is the energy loss due to polarization, and $E_{\text{ex}}$ is the exciton binding energy. From this relationship, it can be found that the optical band gap corresponds to exciton gap and is obtained from optical absorption, whereas transport band gap refers to the
gap separating the electron and hole transport level. Optical band gap is smaller than the transport band gap.

2.4 Excitons

2.4.1 Classification of Excitons

Due to the strong tendency of localization of charge carriers, light absorption or charge injection in organic semiconductors leads to the creation of excitons, or bound electron-hole pairs, instead of free electrons and holes as in inorganic semiconductors. The excitons are the excited states of the molecules and can be treated as chargeless particle capable of diffusion.

![Figure 2-7](image)

Figure 2-7. Schematic illustration of three types of excitons in a solid:\textsuperscript{121} A) Frenkel exciton, localized on single molecule; B) Charge-transfer exciton, slightly delocalized over two or several adjacent molecules; C) Wannier-Mott exciton, highly delocalized with a radius much greater than the lattice constant.

There are three types of excitons in solids based on different extent of charge delocalization: the Frenkel exciton, charge-transfer exciton, and Wannier-Mott exciton, as shown in Figure 2-7.\textsuperscript{121} The Frenkel exciton has the electron and hole localizing on the same molecule for the excited state. And the radius of the exciton is less than or close to the lattice constant. With the increasing intermolecular interactions, the excited
state may delocalize over two or several adjacent molecules, forming the charge-transfer (CT) exciton. Frenkel and CT excitons are typically present in organic semiconductors. For the conventional inorganic semiconductors, the highly delocalized hydrogen-like Wannier-Mott excitons with a radius much greater than the lattice constant are commonly found. Due to the Coulombic interaction between the constituent electron and hole, the Frenkel or CT excitons are tightly bound, with a binding energy ranging from 0.1 to 2 eV,\textsuperscript{122-124} while that for Wannier-Mott excitons in inorganic semiconductors is only a few meV.\textsuperscript{125}

Similar to the transport of single carriers, exciton migration or diffusion among the same species of molecules can occur through band transport or hopping process. The weak intermolecular interactions also lead to a limited exciton mobility in organic semiconductors.

### 2.4.2 Multiplicity of Excitons

Based on the spin statistics, the symmetric and anti-symmetric wave functions ($\Psi_s$ and $\Psi_a$, respectively) of the excited state for a two-electron system can be expressed as:

$$
\Psi_s = \chi_1(\uparrow)\chi_2(\uparrow)
\Psi_s = \chi_1(\downarrow)\chi_2(\downarrow)
\Psi_s = \chi_1(\uparrow)\chi_2(\downarrow) + \chi_1(\downarrow)\chi_2(\uparrow)
\Psi_a = \chi_1(\uparrow)\chi_2(\downarrow) - \chi_1(\downarrow)\chi_2(\uparrow)
$$

where, $\chi_n$ (n=1,2) is the spin function of electron, and (\uparrow) or (\downarrow) represent the possible spin states of electron. For the states of symmetric $\Psi_s$, the spin states of the two electrons are parallel and the total spin $S = 1$, while the two electrons have the opposite spin states for the state of anti-symmetric $\Psi_a$ with the total spin $S = 0$. So if the formation
The probability of singlet and triplet excited state is identical, then the ratio of singlet and triplet excitons can be expected to be 1:3, which means the singlet only comprise 25% of the excitons. Figure 2-8 shows the radiative relaxation processes of fluorescence and phosphorescence from singlet and triplet excitons, respectively. Triplet excited state has lower energy because it is spatially symmetric under exchange of electrons. As shown in Figure 2-8, fluorescence decays from singlet excited state to the ground state with conserved symmetry and is usually a very fast (~10^{-9} s) process. Disallowed by the symmetry, phosphorescence decays from the triplet excited state to the ground state slowly (1 ms to 1 s).

![Figure 2-8](color) Schematic illustration of fluorescence (decay from the singlet exciton, left) and phosphorescence (decay from the triplet exciton, right). (Courtesy of V. Bulovic)

### 2.4.3 Metal-Ligand Charge Transfer Exciton

The singlet and triplet excited states need to be mixed to make both singlet and triplet decay allowed, so that all the excitons can contribute to the radiative emission. This can be achieved by utilizing metal-organic complexes with heavy transition metals.
such as iridium (Ir), platinum (Pt), osmium (Os), and ruthenium (Ru), due to very strong spin-orbit coupling which is proportional to the atomic number ($Z^4$) of heavy metals.

![Figure 2-9. (color) Two types of metal-organic phosphors with heavy transition metals. A) Type I: exciton localized on organic ligand; B) Type II: metal-ligand charge transfer exciton (MLCT).](image)

There are two types of metal-organic phosphors based on the different extent of spin orbit coupling, as shown in Figure 2-9. For the Type I phosphor such as Pt-complex, excitons are localized within the organic ligands with less singlet and triplet states mixing. Heavier transition metals such as Ir can effectively enhance the state mixing, generating emissive metal-ligand charge transfer (MLCT) excitons, which delocalize among the metal atom and organic ligands. This Type II phosphor has much lower triplet lifetime (~1 µs) than the less mixing Type I phosphor (~100 µs) due to the spin orbit coupling. Therefore, it is theoretically possible to convert all the singlet and triplet excitons to phosphorescence, leading to almost 100% photon conversion efficiency by using these organometallic compounds as emitters.

### 2.5 Intra-Molecular Energy Transfer

After the excitons are formed, there are several routes for the excitons to relax back to the ground state ($S_0$) within the same species of molecule. Figure 2-10 shows the electronic states of a molecule and the possible transition process between them.
This energy diagram is also called Jablonski diagram. In this diagram, the electronic states are arranged vertically by energy and grouped horizontally by spin multiplicity.

The vibrational ground states of each electronic state are indicated with thick lines, the higher vibrational states with thinner lines. Non-radiative transitions are indicated by squiggly arrows and radiative transitions by straight arrows. The time scale for each transition is also indicated. The Jablonski diagram shows what sorts of transitions that can possibly happen in a particular molecule. Each of this possibility is dependent on the time scale of each transition. The faster the transition, the more likely it is to happen as determined by selection rules.

Figure 2-10. (color) Jablonski energy diagram.\textsuperscript{127} The electronic states are arranged vertically by energy and grouped horizontally by spin multiplicity (singlet: S, triplet: T). The vibrational ground states of each electronic state are indicated with thick lines, the higher vibrational states with thinner lines. Non-radiative transitions are indicated by squiggly arrows and radiative transitions by straight arrows. The time scale for each transition is also indicated. IC and ISC are referred to internal conversion and intersystem crossing, respectively.
2.5.1 Absorption

The absorption process occurs with excitation energy of photon ($h\nu$) larger than the band gap, and there is a series of wavelengths that can lead to a transition from the ground state to the excited states ($S_0 \rightarrow S_{1,2}$). Thus, electronic absorption spectra generally show the broad bands, rather than the single lines. Absorption transition is a very fast process, on the order of $10^{-15}$ s.

2.5.2 Vibrational Relaxation and Internal Conversion

Once the electron on the ground state is excited to the higher energy excited states by the absorption of photon, the exciton is generated. There are several ways that the energy may be dissipated. The first is through vibrational relaxation, which is a non-radiative process. This relaxation occurs between different vibrational states within the same electronic state. The dissipated energy through the vibrational relaxation may stay within the same molecule, or it may be transferred to other molecules around the excited molecule, depending on the phase of the probed sample. This process is also very fast ($10^{-14}$-$10^{-10}$ s), so it is very likely to occur immediately following absorption.

A transition may also happen from a vibrational state in one electronic state to another vibrational state in a lower electronic state, which is called internal conversion (IC). Internal conversion occurs because of the overlap of vibrational and electronic states and is mechanistically identical to vibrational relaxation.

The molecular spin state remains the same for both vibrational relaxation and internal conversion transitions.

2.5.3 Intersystem Crossing

The radiationless transition between different vibrational states with different spin multiplicity is another path for the dissipation of energy, called intersystem crossing
(ISC). In this process, a singlet excited state non-radiatively transfers to a triplet excited state, or the corresponding converse process from a triplet excited state to a singlet excited state. The probability of this transition occurring is more favorable when the vibrational levels of the two excited states overlap, since little or no energy will be gained or lost in the transition. Intersystem crossing is most common in heavy-atom containing molecules due to the spin orbit coupling effect.

2.5.4 Fluorescence

Once excitons are generated, they quickly relax to the lowest vibrational level of an excited singlet state via vibrational relaxation or internal conversion processes. Then excitons can radiatively decay from the singlet excited state to the ground state \((S_1 \rightarrow S_0)\) with conserved symmetry, called fluorescence. Fluorescence can only exploit the singlet excitons (about 25% of the total excitons) and has a short radiative lifetime of approximately \(10^{-9}\) to \(10^{-6}\) s. Delayed fluorescence may happen as the triplet excited state transfer back to the singlet excited state via intersystem crossing, leading to the emissive transition to the ground state.

2.5.5 Phosphorescence

In the intersystem crossing transition, the singlet excited state non-radiatively transfers to the triplet excited state. The triplet excited state then undergoes the internal conversion and falls to the lowest vibrational level of the triplet electronic state. The radiative transition from the lowest vibrational level of the triplet electronic state to the ground state \((T_1 \rightarrow S_0)\) is possible with strong spin-orbit coupling. This transition is called phosphorescence and is a very slow process, on the order of \(10^{-3}\) to 1 s. The molecules are therefore able to emit slowly after the excitation.
2.5.6 Frank-Condon Shift

Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. During an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

![Energy Diagram](image)

Figure 2-11. Frank-Condon principle energy diagram. The vibronic transitions in a molecule with Morse-like potential energy functions in both the ground and excited electronic states are shown. (Courtesy of J. Xue)

Figure 2-11 show the energy diagram of Frank-Condon principle. The absorption is dominated by transition from the zero order vibrational mode of ground state to the higher order vibrational mode of the excited state ($S_{a0} \rightarrow S_{a2^*}$). The excited electrons then undergo a fast vibrational relaxation by releasing heat to the zero order mode ($S_{a2^*} \rightarrow S_{a0^*}$). Light emission occurs from transition of the zero order vibrational mode of the excited state to various vibrational modes of the ground state ($S_{a0^*} \rightarrow S_{c1}$).
So there exists difference between the absorption excitation energy and emission photon energy, which leads to the red-shifted emission peak compared to the absorption peak,\textsuperscript{128} called Frank-Condon shift.

### 2.6 Inter-Molecular Energy Transfer

Inter-Molecular energy transfer between a donor molecule (initial exciton site) and an acceptor molecule (final exciton site) may occur through photon re-absorption, Förster energy transfer or Dexter energy transfer. For the first process, the photon emitted by recombination of the exciton on the donor molecule is re-absorbed by the acceptor molecule. This process is a radiative transfer and may occur at long distances, typically more than 100 Å. An overlap in the emission spectrum of the donor molecule and the absorption spectrum of the acceptor molecule is required. The latter two processes are non-radiative energy transfers. The mechanisms of Förster and Dexter energy transfers are illustrated in Figure 2-12.

#### 2.6.1 Förster Energy Transfer

Förster energy transfer\textsuperscript{129} also depends upon the spectral overlap, however, no photon is actually emitted. Rather, the dipole-dipole interaction between the donor and acceptor molecules induces a resonant transition of the donor molecule to the ground state and the acceptor molecule to the excited state, as shown in Figure 2-12. Förster energy transfer happens very fast (< 10\textsuperscript{-9} s) typically in singlet-singlet transitions. The distance over which Förster energy transfer occurs may be up to 100 Å, shorter than that for the photon re-absorption process due to the strong distance dependence of the dipole-dipole interaction. The Förster energy transfer rate constant is given by:\textsuperscript{114,130}

\[
k_{D\rightarrow A} = \frac{K^2 J \cdot 8.8 \times 10^{-28} \text{mol}}{n^4 \tau_D r^6}
\]
where $K$ is an orientation factor, $n$ is the refractive index of the medium, $\tau_D$ is the radiative lifetime of the donor, $r$ is the distance (cm) between donor and acceptor, and $J$ is the spectral overlap (in coherent units: cm$^6$-mol$^{-1}$) between the absorption spectrum of the acceptor and the fluorescence spectrum of the donor.

![Diagram](image)

Figure 2-12. (color) Schematic illustration of two non-radiative inter-molecular energy transfer processes between host and dopant: (left) Förster energy transfer with long range interaction (~30-100 Å); (right) Dexter energy transfer with short range interaction (~6-20 Å). The typical transition types are also indicated. (Courtesy of J. Xue)

### 2.6.2 Dexter Energy Transfer

Dexter energy transfer involves bilaterally electron exchange between molecules, as shown in Figure 2-12. The exchange mechanism typically occurs within a very short range of ~10 Å and allows for the singlet-singlet and triplet-triplet transitions. Unlike the six-power distance dependence of Förster energy transfer, the transfer rate constant of Dexter energy transfer exponentially decays as the distance between the two molecules increases. The transfer rate constant, $k_{ET}$, is given by:

$$k_{ET} = \frac{\hbar}{2\pi P^2} \cdot J \exp[-2r/L]$$
where \( r \) is the distance between donor and acceptor, \( L \) and \( P \) are constants not easily related to experimentally determinable quantities, and \( J \) is the spectral overlap integral. For this mechanism the spin conservation rules are obeyed.

### 2.6.3 Exciton Dissociation

An exciton may also dissociate into a free electron and hole when it is subject to an electric field or at heterointerfaces. Due to the large exciton binding energy, an intense electric field of \( 10^6 \) V/cm is needed to cause only a small fraction of Frenkel excitons to dissociate.\(^{131}\) Alternatively, heterojunctions between organic materials with different electron affinities and ionization potentials, and structural and chemical defects present in these materials, may provide efficient exciton dissociation sites for rapid charge-transfer. For example, exciton dissociation at an organic heterojunction between a donor with a low ionization potential and an acceptor with a high electron affinity may be energetically favorable, leading to electrons in the LUMO of the acceptor and holes in the HOMO of the donor.\(^{131,132}\) Such a donor-acceptor heterojunction structure is used in organic photovoltaic cells.
CHAPTER 3
FUNDAMENTALS OF ORGANIC LIGHT-EMITTING DEVICES

3.1 Device Structure of OLEDs

OLED architecture can be divided into two groups depending on the light-emitting direction, the bottom-emitting OLED (BOLED) and the top-emitting OLED (TOLED). General device structures of both types of OLEDs are shown in Figure 3-1. In the conventional BOLED structure, light is directed out from the emissive layer (EML) to the air through the semi-transparent anode and transparent glass substrate (bottom-direction), as opposed to the TOLED, in which the light is directed out through the semi-transparent cathode to the air (top-direction). The light hit the opaque electrodes (that is cathode for BOLED, and anode for TOLED) will be reflected back to the opposite directions.

Figure 3-1. (color) Typical structures of OLEDs: (Left) the bottom-emitting OLED (BOLED) and (Right) the top-emitting OLED (TOLED). Here HTL = hole transporting layer, ETL = electron transporting layer, and EML = emissive layer.

Indium tin oxide (ITO) is generally used as an anode with high transmittivity (~90%) to visible light and low sheet resistance (~20 Ω/□) patterned on the glass substrate for
typical BOLED. ITO has high treatment-sensitive work function, which promotes injection of holes into the HOMO level of the successive organic layer. Usually in the OLEDs based on polymer EMLs (PLEDs), a layer of polythiophene derivative doped with polystyrene sulfonic acid, PEDOT:PSS, is also deposited after ITO to enhance the hole injection.\textsuperscript{133} PEDOT:PSS is the $p$-type conducting polymer with HOMO level of 4.8~5.2 eV, and has a high lateral conductivity and also transparent over the visible spectrum. The chemical structures of PEDOT:PSS are shown in Figure 3-2.

![PEDOT-PSS Chemical Structures](image)

**Figure 3-2.** Chemical structures of Poly(3,4-ethylenedioxythiophene) (PEDOT) and Poly(styrenesulfonate) (PSS).

A hole transporting layer (HTL) facilitates hole injection from the anode to the emissive layer (EML), and also functions as an electron blocking layer (EBL) and helps confine excited states to the EML. Similarly, the electron transporting layer (ETL) helps better electron injection from the cathode to the EML, typically with a thin electron injection layer (EIL) between the ETL and the cathode. Injected holes and electrons from the anode and cathode, respectively, recombine and create excitons in the EML, and emit the light depending on the band gaps of emitters, via the radiative relaxation process. Highly reflective metals such as silver (Ag) and aluminum (Al) can be typically used as the cathode materials in BOLED due to their high reflectivity and low work
functions (4.1~4.2 eV). In this dissertation, the BOLED structure will be mainly employed and discussed.

3.2 Fabrication of OLEDs

BOLEDs are typically fabricated on glass substrates commercially pre-coated with an indium tin oxide (ITO) anode (sheet resistance ~ 20 Ω/□). A typical way to clean the substrates are, place the substrates in ultrasonic baths of deionized water, acetone, and isopropanol consecutively, sonicing for 15 minutes each, and are then exposed to the ultraviolet ozone ambient for 15 minutes immediately before the next processing step.

Depending on the molecular weight of the organic molecules which are used for the thin film growth, OLEDs can be divided into two types; small-molecule OLEDs (SMOLEDs) and polymer OLEDs (PLEDs). Small molecule is defined by a molecular weight less than 1000 g/mol, whereas polymer has long and complicated structures with the molecular weight approximately more than 1000 g/mol. There have been many different methods to grow organic thin films including small molecules thin films deposition methods such as vacuum thermal evaporation (VTE), organic vapor phase deposition (OVPD), organic vapor jet printing (OVJP), and organic molecular beam deposition (OMBD), and polymer thin films deposition methods such as spin coating, spraying method, inkjet printing, and even the roll-to-roll processing. Among those methods, for research in the laboratory, VTE is commonly used to fabricate SMOLEDs, whilst the spin-coating is most widely used for deposition of PLEDs.

Figure 3-3A illustrates the VTE system in which the main vacuum chamber is pumped to the typical pressure under $10^{-6} \sim 10^{-7}$ Torr. The source boat placed in the bottom of the vacuum chamber is electrically heated up and organic materials in the source boat are sublimed in a vacuum environment. The ballistic molecular thin film
deposition is possible with tens of centimeter scale mean free path under the ultra-high vacuum in the chamber, larger than the chamber size and therefore avoiding the collision of molecules when traveling from source boat to substrate. A quartz crystal monitor (QCM, coated with a thin gold layer) provides film thickness control with accuracy up to 0.1 Å/s. The patterning of organic and metal deposition can be realized by using shadow masking.

The VTE method provides several advantages of the organic thin films deposition for OLEDs fabrication. It has very clean environment with low impurity incorporated, due to the ultra-high vacuum during the deposition process. It is also capable of depositing multi-layers, mixed or doped layers, and metal layers. But the VTE method is only applied to relatively small area OLEDs, due to the poor uniformity of large area film thickness, considerable waste of source materials and challenging patterning for large area films. The shadow masks and chamber wall need to be routinely cleaned.

Figure 3-3. (color) Schematic illustration of organic thin film growth processes: A) Vacuum thermal evaporation (VTE) for small molecules thin film deposition and B) Spin-coating for polymer thin film deposition.
Figure 3-3B schematically shows the spin-coating process where polymers are dissolved in a specific solvent and dropped onto the substrate, which rotates at an angular velocity. Centrifugal forces spread the solution over the surface of substrate, and a thin layer of polymer film will be formed as the solvent evaporates. A thermal annealing process is typically required to completely evaporate the solvent residue and further densify the coating after spin-coating. The thickness of a polymer thin film can be accurately controlled by adjusting the spin speed and the polymer concentration in the solution. Benefits of spin coating include fast process time and high uniformity of thin films. Similar to the VTE method, spin coating can only be used for relatively small area PLEDs and the waste of solution also cannot be neglected. Spin coating method cannot deal with the metal deposition, so other methods such as VTE method need to be used to finalize the device fabrication.

Finally, the encapsulation of device is not required for OLEDs research in the laboratory, but will definitely increase the stability of devices for longer duration.

### 3.3 Principle of OLEDs Operation

Figure 3-4 illustrate the energy band diagrams for the operation processes of the OLED. The OLED is simplified as a single organic layer structure sandwiched by the anode and the cathode in each side for electrical contacts. Fermi levels ($E_F$) of organic layers are not aligned before the electrical contact with anode and cathode, as shown in Figure 3-4A. After the electrical contact, there is a thermal equilibrium state with aligned $E_F$. However, charge injection into the organic layer is still not preferable due to the built-in potential barrier shown in Figure 3-4B.

When the voltage bias is applied to the electrodes, charge carriers are ready to be injected into the organic layer at $V = V_{bi}$, as shown in Figure 3-4C. When applied voltage
bias, $V > V_{bi}$, charge carriers are then injected into the organic layer, as shown in Figure 3-4D. Holes move upward through the HOMO level and electrons transport downward through the LUMO level of the organic layer, respectively. Excitons are formed once both types of charge carriers meet with each other in the organic layer, and energetically bounded together (Coulombic interaction). The radiative recombination of excitons in the organic layer will generate light emission. The wavelength of the light emission depends on the band gap of the material in the organic layer.

Figure 3-4. (color) Schematic energy band diagrams of OLEDs operation. A) before the electrical contact, B) after the electrical contact but no voltage bias applied, C) with voltage bias applied through the OLED, and charge carriers ready to be injected at $V = V_{bi}$, and D) charge carriers injected into the organic layer at $V > V_{bi}$, and light emitted by the recombination of excitons.
3.4 Electromagnetic Spectrum

The electromagnetic (EM) spectrum is the range of all possible wavelengths (frequencies) of electromagnetic radiation, as shown in Figure 3-5. The EM spectrum extends from low frequencies used for modern radio communication to gamma radiation at the high-frequency end. Light is defined as visible radiation of electromagnetic waves which can be observed by the human eyes, and located in the wavelength ranges between 380 nm and 770nm. The visible spectrum can be further subdivided according to different colors, with red at the long wavelength end and violet at the short wavelength end, as illustrated in the inset of Figure 3-5. White light is a combination of lights of different wavelengths in the visible spectrum.

![Electromagnetic Spectrum Diagram](image)

Figure 3-5. (color) The electromagnetic spectrum as a function of wavelength (nm). The visible spectrum is further specified.

Next in frequency comes ultraviolet (UV) radiation. The wavelength of UV rays is shorter than the violet end of the visible spectrum but longer than the X-ray. UV rays are very energetic due to the short wavelengths. In this dissertation, OLEDs with emission spectra covering from blue, violet in visible spectrum to UV will be studied.
The infrared (IR) part of the EM spectrum comes after the red part of the visible spectrum in wavelengths. It covers the range from roughly 750 nm to 1 mm, and can be divided into three ranges: far-infrared, mid-infrared, and near-infrared. This dissertation will focus on the OLEDs emitting near-infrared radiation with spectrum range from 750 nm to 2500 nm.

<table>
<thead>
<tr>
<th>Photometric (Visible Light: 380-770 nm)</th>
<th>Radiometric (Entire Electromagnetic Spectrum)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Illuminance</strong> [lx] = [lm/m^2]</td>
<td><strong>Irradiance</strong> [W/m^2]</td>
</tr>
<tr>
<td><strong>Luminous Flux</strong> [lm]</td>
<td><strong>Radiant Flux</strong> [W]</td>
</tr>
<tr>
<td><strong>Luminous Intensity</strong> [cd] = [lm/sr]</td>
<td><strong>Radiant Intensity</strong> [W/sr]</td>
</tr>
<tr>
<td><strong>Luminance</strong> [cd/m^2] = [lm/sr-m^2]</td>
<td><strong>Radiance</strong> [W/sr-m^2]</td>
</tr>
<tr>
<td><strong>Luminance Efficiency</strong> [cd/A] = [lm/sr-A]</td>
<td><strong>Radiance Efficiency</strong> [W/sr-A]</td>
</tr>
<tr>
<td><strong>Luminous Power Efficiency</strong> [lm/W]</td>
<td><strong>Power Efficiency</strong> [W/W]</td>
</tr>
</tbody>
</table>

Figure 3-6. Comparison between Photometry and Radiometry. The terminologies and their corresponding SI units for Photometry and Radiometry are listed.

### 3.4.1 Photometry vs. Radiometry

Photometry is defined as the science of the measurement of light in visible spectrum wavelengths (\( \lambda = 380-770 \) nm), whereas Radiometry is the science of measurement of radiant energy in terms of absolute power, and can be applied to the entire spectrum of electromagnetic radiation.\[141\] The terminologies and their corresponding units for photometry and radiometry are summarized in Figure 3-6. A
primary distinction between Photometry and Radiometry is, radiant flux uses [Watt] as the unit, but luminous flux uses [Lumen] as the unit. In photometric quantities, every wavelength is weighted according to how sensitive the human eye is to it, while radiometric quantities use unweighted absolute power. Since in this dissertation, we will focus on OLEDs with near-infrared and ultraviolet emission, therefore, the more general concept Radiometry will be used.

3.4.2 Photopic vs. Scotopic Response

The illuminance at daytime is about 100,000 lux (lx), as opposed to about 0.0003 lx at night. In order to detect such a wide range of illuminance, the size of the pupil and the responsivity of the retina of the human eye changes according to the brightness of the environment. The human eye has different responses as a function of wavelength when it is adapted to light conditions and dark conditions. In a relatively bright environment (> 3 cd/m$^2$), the human eye detects the light based on the photopic response, while scotopic response is dominant in the dark conditions (< 0.0003 cd/m$^2$). Mesopic response occurs in intermediate lighting conditions and is effectively a combination of scotopic and photopic vision.

As shown in Figure 3-7, the photopic response, $G(\lambda)$, has the peak luminous power efficiency of $\phi_0 = 683$ lm/W at $\lambda = 555$ nm, whereas the scotopic response, $G'(\lambda)$, has the blue-shifted peak value of $\phi_0' = 1700$ lm/W at $\lambda = 507$ nm, and insensitive to the wavelengths longer than approximately 640 nm (red). So, the photopic and scotopic responses can be expressed as:

$$G(\lambda) = \phi_0 \times g(\lambda)$$
$$G'(\lambda) = \phi_0' \times g'(\lambda)$$
where \( g(\lambda) \) and \( g'(\lambda) \) are the normalized photopic and scotopic responses, respectively.

Figure 3-7. Photopic and scotopic responses of human eye. The vertical axis is plotted as luminous efficacy in \( \text{lm/W} \).

### 3.4.3 Plane vs. Solid Angles

For the application of photometry and radiometry, the concept of solid angle, instead of the widely known plane angle, is usually used.

Figure 3-8. Plane and solid angles: A) a plane angle \( \theta \) in 2-D and B) a solid angle \( \Omega \) in 3-D. Here, \( r \) is the radius of the circle or sphere; \( L \) is the length of arc in the circle; and \( A \) is an arbitrary spherical surface area. (Courtesy of S. -H. Eom)
As shown in Figure 3-8, a plane angle (θ) is defined as a ratio of the length of the arc to the radius of the circle in two-dimensional space, whereas a solid angle (Ω) is defined as a ratio of the spherical surface area to the square of the radius of the sphere in three-dimensional space. The SI units for the plane angle and solid angle are radian (rad) and steradian (sr), respectively. In spherical coordinates, the solid angle can be expressed as:

$$\Omega = \int \frac{dA}{r^2} = \iint_A \sin \theta d\theta d\varphi$$

### 3.4.4 Lambertian Emission Source

An isotropic light emitting with equal radiance (luminance) into a ny solid angle is defined as a Lambertian source.

An important property for the Lambertian source is the cosine law that, the radiance (luminance) is exactly the same when a Lambertian source is viewed from any angle. This is because although the emitted power from a given area element is reduced by the cosine of the emission angle, the apparent size (solid angle) of the

Figure 3-9. (color) Schematic illustration of a Lambertian emission with equal radiance into any solid angles.\textsuperscript{143} A) Emission from an area element (dA) in a normal and angle θ direction; B) Observing from normal and angle θ direction.
observed area, as seen by the viewer, is also decreased by a corresponding amount. Therefore, the radiances are the same.

This can be further quantitatively demonstrated as illustrated in Figure 3-9. Suppose the radiance along the normal of the circle is \( I \) (energy per unit solid angle per projected source area). So, the radiance emitted into the vertical wedge and wedge at angle \( \theta \) both with solid angle of \( d\Omega \) is, \( I d\Omega dA \) and \( I \cos(\theta)d\Omega dA \), respectively, as shown in Figure 3-9A. From the view of observer, the observer directly above the area element \( dA \) will see the scene through an aperture of area \( dA_0 \) and the area element will subtend a solid angle of \( d\Omega_0 \), as shown in Figure 3-9B. So this normal observer will then record the radiance as:

\[
I_{\text{normal}} = \frac{Id\Omega dA}{d\Omega_0 dA_0}
\]

Similarly, the observer at angle \( \theta \) to the normal will be seeing the scene through the same aperture \( (dA_0) \) and the area element will subtend a solid angle of \( d\Omega_0 \cos(\theta) \). Then the observer will record the radiance as:

\[
I_{\theta} = \frac{I \cos(\theta)d\Omega dA}{d\Omega_0 \cos(\theta)dA_0} = \frac{Id\Omega dA}{d\Omega_0 dA_0}
\]

which is the same as what the normal observer has seen.

### 3.4.5 CIE Color Space

The Commission Internationale de L’Eclairage (CIE) color space was created in 1931, and can be defined by the tristimulus values of \( X, Y, \) and \( Z \). The human eye has photoreceptor (called cone cells) with sensitivity peaks in short (\( S, 420-440 \) nm), middle (\( M, 530-540 \) nm), and long (\( L, 560-580 \) nm) wavelengths. The tristimulus values of a color are the amount of three primary colors needed to match that test color. The
CIE color space has defined a set of three color-matching functions, call \( x(\lambda) \), \( y(\lambda) \), and \( z(\lambda) \), as shown in Figure 3-10. The tristimulus values \((X, Y, Z)\) for color with a spectral power distribution \( S(\lambda) \) are given in terms of the color-matching functions by:

\[
X = \int_{0}^{\infty} S(\lambda) x(\lambda) d\lambda \\
Y = \int_{0}^{\infty} S(\lambda) y(\lambda) d\lambda \\
Z = \int_{0}^{\infty} S(\lambda) z(\lambda) d\lambda
\]

Figure 3-10. (color) Color-matching function curves: \( x(\lambda) \), \( y(\lambda) \), and \( z(\lambda) \).\(^{142}\) The tristimulus values of \((X, Y, Z)\) can be obtained by integrating the color-matching function curves.

Since the human eye has three types of color sensors that respond to different ranges of wavelengths, a full plot of all visible colors is a three dimensional figure. However, the CIE color space was deliberately designed so that the \( Y \) parameter was a measure of the brightness of color, while the chromaticity of a color was then specified by the two derived parameters, \( x \) and \( y \), as the functions of three tristimulus values \( X, Y, \) and \( Z \):
This derived color space specified by \( x \), \( y \), and \( Y \) is known as the CIE \( xyY \) color space and leads to the widely used two dimensional CIE chromaticity diagram, as shown in Figure 3-11.

![Figure 3-11. (color) CIE chromaticity diagram represented by \((x,y)\) coordinates. Planckian locus (black body radiation) is also illustrated with lines of constant correlated color temperature \((T_c)\).](image)

The diagram represents all of the chromaticities visible to the average person. The horseshoe-shaped region shown in colors is called the gamut of human vision. The outer curved boundary is the spectral locus and corresponds to monochromatic light.
(each point representing a pure hue of a single wavelength), with wavelengths shown in nanometers. The lower part on the border of the gamut, without counterpart in monochromatic light, is called line of purples. The chromaticities of black body light sources of various temperatures and lines of constant correlated color temperature \((T_c)\) are also shown in Figure 3-11.

Note that the chromaticity diagram is a tool to specify how the human eye will experience light with a given spectrum. It cannot specify colors of objects since the chromaticity observed while looking at an object depends on the light source as well.

3.5 Characteristics of OLEDs

The accurate and consistent measurement of OLED characteristics is important for comparison among different research groups and different devices. A measurement method for the OLED has been suggested previously. The measurement method, definitions, and calculations in this dissertation are based on the previous suggested report and equipment in one specific research laboratory. Although the available equipment and measurement set-up might be somewhat different among different research groups, it can provide a consistent device result comparison by following the similar understanding of fundamental concepts.

Radiant emittance \((R)\) or luminance \((L)\) – current density \((J)\) – voltage \((V)\) characteristics of the OLEDs were measured in ambient using an Agilent 4155C semiconductor parameter analyzer and a calibrated silicon detector (Newport 818 UV). The luminance was calibrated using a Konica Minolta LS-100 luminance-meter (with No. 110 close-up lens). The Lambertian emission source is assumed for both radiant emittance and luminance calibration. Electroluminescent (EL) spectra were taken using the corresponding spectrometers for devices with different range emission.
The spectrum with absolute power intensity can be obtained by the EL spectra measurement, written by the following expression:

\[ I(\lambda) = I_0 \cdot S(\lambda) \]  

where \( I(\lambda) \) is the spectrum with absolute power intensity, [W]; \( S(\lambda) \) is the normalized spectrum with amplitude constant of \( I_0 \).

The semiconductor parameter analyzer will record the photo-current by using the silicon photo-detector. The photo-current, \( I_{\text{det}} \), can be written as:

\[ I_{\text{det}} = \int I_{\text{det}}(\lambda)d\lambda \]  

where \( I_{\text{det}}(\lambda) \) is the photo-current at a single wavelength of \( \lambda \), [A]. Then the spectrum with absolute power intensity can be re-written as:

\[ I(\lambda) = I_0 \cdot S(\lambda) = \frac{1}{f} \cdot \frac{I_{\text{det}}(\lambda)}{R(\lambda)} \]  

where \( f \) is the geometry factor, which is the fraction of photons reaching the photo-detector comparing to the total photons emitted by the OLEDs; \( R(\lambda) \) is the responsivity of the photo-detector, [A/W]. By replacing the term of \( I_{\text{det}}(\lambda) \) in Equation 3-2, the photo-current can be then re-written as:

\[ I_{\text{det}} = \int I_{\text{det}}(\lambda)d\lambda = \int fI_0 S(\lambda)R(\lambda)d\lambda = fI_0 \xi \]  

where \( \xi = \int S(\lambda)R(\lambda)d\lambda \)  

By replacing \( I_0 \) in Equation 3-1, \( I(\lambda) \) can be further re-written as:

\[ I(\lambda) = I_0 \cdot S(\lambda) = \frac{I_{\text{det}}}{f\xi} \cdot S(\lambda) \]
Both Equation 3-4 and 3-6 show the relation between the measured spectrum and photo-current. Based on the data sets from the $R$-$J$-$V$ or $L$-$J$-$V$ characteristics and EL spectrum measurement, all the properties of OLEDs can be derived as follows.

3.5.1 Radiance

Radiance ($R_v$) is defined as the radiant flux per unit area per unit solid angle (or radiant intensity per unit area). The unit for radiance is [W/sr-m²] and it characterizes the total emission power emitted by the sources. Another term, radiant emittance ($R$), does not consider the solid angle in a specified direction emitted from the sources, and the unit is [W/m²]. Based on the definition, the radiant emittance can be expressed as:

$$ R = \frac{\int I(\lambda)d\lambda}{A} \quad (3-7) $$

where $A$ is the device area. Substituted the $I(\lambda)$ with Equation 3-6:

$$ R = \frac{\int I(\lambda)d\lambda}{A} = \frac{1}{Af} \cdot \int \frac{S(\lambda)d\lambda}{\xi} \cdot I_{det} \quad (3-8) $$

In this dissertation, the term radiant emittance ($R$) and unit of [W/m²] will be used.

3.5.2 Luminance

Luminance ($L$) is defined as the luminous flux per unit area and per unit solid angle (or luminous intensity per unit area) and the unit for luminance is [cd/m²] (= [lm/sr-m²] or [nit]). Different from the radiance which only considers the total power of emission, luminance needs to incorporate the photopic response of human eyes. So the expression of luminance can be written as:

$$ L = \frac{\int G(\lambda)I(\lambda)d\lambda}{A\pi} = \frac{\phi_0}{A\pi f} \cdot \int \frac{g(\lambda)S(\lambda)d\lambda}{\xi} \cdot I_{det} = \alpha \cdot I_{det} \quad (3-9) $$
where \( \alpha = \frac{\phi_0}{A \pi f} \cdot \int g(\lambda)S(\lambda)d\lambda \) \( \xi \) 

Equation 3-9 and 3-10 are also used for the calibration of geometry factor, \( f \).

3.5.3 Luminance Efficiency

Luminance efficiency (\( \eta_L \)) is also called current efficiency and it is defined as a ratio of luminance to the injected current density to the OLED, \( J_D \), as expressed in Equation 3-11. The unit of \( \eta_L \) is [cd/A].

\[
\eta_L = \frac{L}{J_D} 
\]  

(3-11)

3.5.4 Power Efficiency

Power Efficiency (\( \eta_P \)) is defined as the ratio of output optical power to the input power driving the OLEDs and the unit of \( \eta_P \) is [W/W]. Power efficiency can be calculated by the following equation:

\[
\eta_P = \frac{\int I(\lambda)d\lambda}{J_DA \cdot V} = \frac{1}{Af} \cdot \frac{\int S(\lambda)d\lambda}{\xi} \cdot \frac{I_{det}}{J_D \cdot V} 
\]  

(3-12)

where \( V \) is the applied voltage of OLEDs, [V].

3.5.5 Luminous Power Efficiency

Luminous power efficiency (\( \eta_{LP} \)) is defined as the ratio of output luminous flux to the input power driving the OLEDs and the unit of \( \eta_{LP} \) is [lm/W]. Similar to the luminance, the photopic response of human eyes needs to be included here and the expression of \( \eta_{LP} \) can be written as:

\[
\eta_{LP} = \frac{\int G(\lambda)I(\lambda)d\lambda}{J_DA \cdot V} = \frac{\phi_0}{Af} \cdot \frac{\int g(\lambda)S(\lambda)d\lambda}{\xi} \cdot \frac{I_{det}}{J_D \cdot V} 
\]  

(3-13)
Also, luminous power efficiency of the OLED has the simple conversion with the luminance efficiency ($\eta_L$) as shown in Equation 3-14:

$$\eta_{LP} = \frac{L}{J_D} \cdot \frac{\pi}{V} = \eta_L \cdot \frac{\pi}{V} \quad (3-14)$$

### 3.5.6 External Quantum Efficiency

The external quantum efficiency ($\eta_{EQE}$) physically means a ratio of the number of photons emitted from the OLED to the number of charge carriers injected into the OLED, and can be expressed as:

$$\eta_{EQE} = \frac{\int \frac{I(\lambda)}{hc/\lambda} d\lambda}{J_D A} = \frac{q}{hc} \cdot \frac{\int \lambda I(\lambda) d\lambda}{J_D A} \quad (3-15)$$

where $q$ is the electric charge, $h$ is Planck’s constant, and $c$ is speed of light. Substituted $I(\lambda)$ with Equation 3-6:

$$\eta_{EQE} = \frac{q}{hc} \cdot \frac{\int \lambda I(\lambda) d\lambda}{J_D A} = \frac{q}{hc} \cdot \frac{\int \lambda S(\lambda) d\lambda}{J_D A} \cdot \frac{I_{det}}{\xi} \quad (3-16)$$

By comparing Equation 3-12 and 3-16, the conversion between power efficiency and external quantum efficiency can be derived as:

$$\eta_{EQE} = \frac{qV}{hc} \cdot \frac{\int \lambda S(\lambda) d\lambda}{\int S(\lambda) d\lambda} \cdot \eta_P \quad (3-17)$$

Similarly, the conversion between luminous power efficiency and external quantum efficiency can be derived as:

$$\eta_{EQE} = \frac{qV}{hc \phi_0} \cdot \frac{\int \lambda S(\lambda) d\lambda}{\int (\lambda S(\lambda)) d\lambda} \cdot \eta_{LP} \quad (3-18)$$
3.6 Efficiency of OLEDs

There are basically four steps for the OLED operation including: 1) injection of electrons and holes; 2) capture to from excitons; 3) radiative decay; 4) light emission. So the efficiency of OLEDs will be composed of the efficiency of each step, as shown by the following expression of quantum efficiency of OLEDs:

\[ \eta_{EQE} = \eta_R \cdot \chi \cdot \phi_{PL} \cdot \eta_{out} \]  

(3-19)

Here, \( \eta_R \) is the charge balance factor indicating the ratio of excitons to charge injected. This efficiency can be easily achieved to unity for OLEDs by balancing the charges injected from the anode and cathode, respectively. Balanced charge injection can maximize the exciton generation in the middle zone of the EML and also minimize the possible non-radiative exciton-polaron (excited charge carrier) quenchings. \( \chi \) is the spin statistics factor indicating the ratio of excitons which can radiatively decay. The fluorescent emission can convert only singlet (25%) excitons into photons, whereas the phosphorescent emission can convert singlet (25%) as well as triplet (75%) excitons into photons, leading to theoretically 100% photon conversion efficiency. \( \phi_{PL} \) is the PL efficiency of organic dye and it depends on the property of that material. The PL efficiency of organic dyes can be as high as over 90% in the solution matrix, but the PL efficiency of solid-state thin film reduces significantly due to strong intermolecular interactions. So, higher PL efficiency can ultimately provide higher device efficiency, but also the higher electroluminescent quantum yield of the emissive layer in the OLED should be optimized by alternatively choosing appropriate host-guest systems and/or adjusting the doping concentration of emissive guest. These three efficiencies can also be summarized as the internal quantum efficiency of OLED, \( \eta_{IQE} \), which is defined as
the ratio of total number of photons generated in the OLED to the total number of electrons injected into the OLED:

\[ \eta_{\text{IQE}} = \eta_R \cdot \chi \cdot \Phi_{\text{PL}} \]  

(3-20)

For the phosphorescent organic dye with 100% PL efficiency, the internal quantum efficiency of 100% can be achieved.

However, the external quantum efficiency of BOLED is typically limited to ~20% due to the limitation of light outcoupling efficiency, \( \eta_{\text{out}} \). The light output from emissive layer in OLEDs will be reduced by absorption losses and wave guiding within the device and its substrate due to total internal reflection (TIR) at multiple interfaces.\(^{34,50}\) The OLED has a multi-layered structure usually consisted of a metal reflector, organic layers, ITO, and a glass substrate. Hence, the isotropic dipoles generated in the emissive organic layer must go through multiple interfaces in order to finally come out to the air.

![Figure 3-12. (color) Three optical modes in bottom-emitting OLEDs (BOLEDs): i) air mode (~20%); ii) glass substrate mode (~30%); and iii) localized plasmonic and organic/ITO wave-guiding mode (~50%). The values in parentheses are the percentage of photons in that mode. (Courtesy of S. -H. Eom)\(^{142}\)](image)

There are three optical modes depending on the different optical confinement mechanisms, as shown in Figure 3-12. The first mode is the organic/ITO wave-guiding
modes where almost 50-60% of the generated photons are confined near the metal cathode and organic/ITO layers due to the strong localized electric field on the metal cathode and TIR mainly at the interface between ITO and glass substrate.\textsuperscript{72,73} The second mode is glass substrate mode, causing approximately 20-30% loss of generated photons. In this mode, photons are trapped and lost in the thick glass substrate due to the TIR at the glass/air interface. Therefore, it is believed that only \(~20\%\) of photons in the third air mode can contribute to the $\eta_{\text{out}}$ in a planar BOLED system.
CHAPTER 4
NEAR-INFRARED ORGANIC LIGHT-EMITTING DEVICES BASED ON
FLUORESCENT DONOR-ACCEPTOR-DONOR OLIGOMERS

4.1 Introduction to the Near-IR OLEDs

Since the first report of near-infrared (NIR) emission from an organic light-emitting device (OLED) based on a lanthanide complex,\textsuperscript{55} there has been considerable interest in the development of materials and devices that exhibit wavelength tunable and efficient light emission in the NIR wavelength region. Such work is of interest for a variety of applications in security and defense, telecommunications, and biomedical sectors.\textsuperscript{56-63} For example, NIR OLEDs could serve as a new class of illuminators for night vision, providing advantages such as light weight, low thermal signature, low power consumption, and compatibility with large area and flexible substrates. Much of the existing work on NIR OLEDs has focused on the use of lanthanide-containing organometallic complexes based on Yb, Nd, and Er.\textsuperscript{55,56,64-73} The metal phthalocyanines (Pc) with emissions at the near-IR range are also used for the device demonstration.\textsuperscript{74,75} However, because of the inherent low efficiency of emission from these complexes, the most efficient OLEDs based on these materials possess external quantum efficiencies (EQE) less than 0.3%. More recently, Thompson and co-workers reported the development of a phosphorescent Pt-porphyrin complex that phosphoresce with high quantum yield at a peak wavelength of $\lambda \approx 770$ nm, and achieved EQE up to 8.5% in the optimized OLEDs.\textsuperscript{88,89} However, the emission of this device is still not as deep as into the near-IR emission range. So, there still remains the need for the development of alternative materials and devices that exhibit wavelength tunable and highly efficient emission at $\lambda > 800$ nm. Table 4-1 summarizes some of the existing near-IR OLEDs in the literature.
Table 4-1. List of some existing near-IR OLEDs based on different near-IR emitters. The maximum radiant emittances ($R$) and external quantum efficiencies ($\eta_{EQE}$) are compared for different devices.

<table>
<thead>
<tr>
<th>Emitters</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$R$ ((\mu\text{W/cm}^2))</th>
<th>$\eta_{\text{EQE}}$ (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln(TPP)TP</td>
<td>977-1570</td>
<td>&lt;1</td>
<td>&lt;0.1%</td>
<td>65,67,68</td>
</tr>
<tr>
<td>Ln(TPP)L(OEt)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPyrPyrPV</td>
<td>800</td>
<td>0.06 (17V)</td>
<td>Low</td>
<td>145</td>
</tr>
<tr>
<td>Ethyne-briged Porphyrin</td>
<td>720, 820</td>
<td>-</td>
<td>0.3%, 0.1%</td>
<td>146</td>
</tr>
<tr>
<td>Ir Complexes</td>
<td>720</td>
<td>319 (20V)</td>
<td>0.1%</td>
<td>76</td>
</tr>
<tr>
<td>CllnPc</td>
<td>880</td>
<td>-</td>
<td>-</td>
<td>74</td>
</tr>
<tr>
<td>PdPc, PtPc</td>
<td>1025, 966</td>
<td>-</td>
<td>0.03%, 0.3%</td>
<td>75</td>
</tr>
<tr>
<td>Pt-TPTBP</td>
<td>772</td>
<td>1200</td>
<td>8.5%</td>
<td>88,89</td>
</tr>
<tr>
<td>Os Complexes</td>
<td>814</td>
<td>65 (17V)</td>
<td>1.5%</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>718</td>
<td>172 (14V)</td>
<td>2.7%</td>
<td></td>
</tr>
</tbody>
</table>

4.2 Donor-Acceptor-Donor Oligomers

$\pi$-conjugated donor-acceptor-donor (DAD) oligomers and polymers have been extensively investigated for their controlled optoelectronic properties that include linear and nonlinear optical effects.\textsuperscript{148,149} When the electron-rich donor and electron-deficient acceptor species are covalently bonded with one another in the DAD molecules, the energy of the highest occupied molecular orbital (HOMO) is controlled by the donor portion, while the lowest unoccupied molecular orbital (LUMO) energy is controlled by the acceptor and, as such, the HOMO-LUMO gap can be easily controlled by carefully selecting the appropriate structures of the donor and acceptor units. By combining strong donors with strong acceptors, a set of DAD oligomers and polymers with narrow HOMO-LUMO gaps has been achieved. In the area of non-linear optics, DAD molecules can provide a large two-photon cross section suggesting possible applications in three-dimensional patterning via photopolymerization and optical limiting.\textsuperscript{150} Reynolds and co-workers have exploited oxidative polymerization for the synthesis of narrow gap polymers, as exemplified by our recent report of electrochemically prepared polymer
films deposited on single-walled carbon nanotube films exhibiting band gaps as low as 0.5 eV,\textsuperscript{151} and demonstrated NIR light emission (albeit weak) with solution prepared narrow gap polymers.\textsuperscript{145} Considering the spectral properties of a set of DAD oligomers prepared in the course of their polymer work, we noted that the oligomers have especially long wavelength optical absorption and efficient photoluminescence (PL), making them excellent candidates as the light emitting species for NIR OLEDs prepared via vacuum deposition methods.\textsuperscript{152,153}

In this chapter, we report NIR OLEDs based on two DAD conjugated oligomers, 4,8-bis(2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)benzo[1,2-c;4,5-c']bis [1,2,5]thiadiazole (BEDOT-BBT) and 4,9-bis(2,3-dihydrothieno[3,4-\texttext{-}b][1,4]dioxin-5-yl)-6,7-dimethyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline (BEDOT-TQMe\textsubscript{2}), as illustrated by the structures in Figure 4-1, which have the same donor component but different acceptor ones. Using tris(8-hydroxyquinoline) aluminum (Al\textsubscript{q}3) as the host in the emissive layer (EML), fluorescent OLEDs based on these two NIR emitters were fabricated by doping BEDOT-TQMe\textsubscript{2} or BEDOT-BBT into the host matrix. By varying the doping concentration of the NIR emitter and the thickness of the electron transporting layer, a maximum EQE of $\eta_{EQE} = 1.6\%$ and a maximum power efficiency of $\eta_P = 7.0$ mW/W are achieved in the optimized devices based on BEDOT-TQMe\textsubscript{2}, in which the electroluminescence (EL) peaks at 692 nm but extends to well above 800 nm. BEDOT-BBT based OLEDs show even longer wavelength emission with a maximum at 815 nm and extending to as far as 950 nm, due to the stronger acceptor (BBT) used in this molecule (which corresponds to a smaller HOMO-LUMO gap than that of BEDOT-TQMe\textsubscript{2}). The maximum efficiencies of the optimized BEDOT-BBT devices were reduced to $\eta_{EQE} = 0.51\%$ and $\eta_P = 2.1$ mW/W.
due to the significantly lower fluorescent quantum yield of the corresponding NIR emitter.

The efficiencies of these optimized fluorescent OLEDs were further increased by two to three times by incorporating a phosphorescent sensitizier in the emissive layer to funnel the triplet excitons formed on the host molecules to the fluorescent emitters, which are not harvested in fluorescent devices. Using this sensitized fluorescence (SF) device architecture,\textsuperscript{154} we achieved maximum efficiencies of $\eta_{\text{EQE}} = 3.1\%$ and $\eta_P = 12$ mW/W for BEDOT-TQMe$_2$ based devices, and $\eta_{\text{EQE}} = 1.5\%$ and $\eta_P = 4.0$ mW/W for BEDOT-BBT based devices. These OLEDs emit with the highest efficiency reported to date for near-IR emitting devices that are based on fluorescent chromophores.\textsuperscript{146,152,153}

The aggregate effect of the donor-acceptor-donor oligomers in the devices is finally studied by utilizing different host matrix and changing the stacking manners of doping molecules. Changing from the previous host of Alq$_3$ to CBP, which has more spectral overlap with the longer emission DAD NIR emitters, the concentration of NIR emitters needed to allow complete energy transfer for excitons on the host molecules will be decreased due to increased Förster radius, leading to less significant aggregate quenching effect. The NIR OLEDs based on BEDOT-BBT doped into CBP host matrix has a maximum EQE of $\eta_{\text{EQE}} = (0.92 \pm 0.07)\%$, which is almost double that of the devices with Alq$_3$ as host. The power efficiency is also higher for the CBP device than the device with Alq$_3$ host, with a maximum of $\eta_P = (3.6 \pm 0.3)$ mW/W for the former device. The effect of molecular structure on aggregation in devices is then studied by adding bulky substituted groups to the two ends of DAD oligomers. However, the NIR OLEDs based on two bulky DAD oligomers show similar aggregate effect, compared to
“bare” BEDOT-BBT based devices. The efficiencies of these bulky DAD oligomers based devices show no enhancement and the emissions are red-shifted with peak wavelengths up to 905 nm.

This chapter is organized as follows. The experimental details on material synthesis, device fabrication and characterization are described in section 4-3. In section 4-4, we present the experimental results and discussion on the optical properties of the DAD oligomers and performance of the fluorescent and sensitized fluorescent devices. We also study the aggregation effect of normal and bulky DAD oligomers in the device in section 4-5. Finally, we conclude in section 4-6.

4.3 Experimental Details

The molecular structures of BEDOT-TQMe₂ and BEDOT-BBT are shown in Figure 4-1. The synthesis of these two DAD oligomers follows a similar process to that reported previously. Briefly, the synthesis started with the bromination of 2,1,3-benzothiadiazole followed by nitration. A Stille coupling between the nitrated product and trimethyltin ethylenedioxythiophene yielded a three-ring precursor which was reduced to the diamine with iron in acetic acid. A final ring closure was done with N-thionylaniline in pyridine or 2,3-butanedione in acetic acid to yield BEDOT-BBT and BEDOT-TQMe₂, respectively. The synthesis of the bulky DAD oligomers follows the same way. The materials were synthesized by Timothy Steckler and Dan Patel in Dr. John Reynolds group in the Department of Chemistry at the University of Florida.

UV-Vis absorption spectra were measured in CH₂Cl₂ solutions using a PerkinElmer Lambda 25 UV-vis spectrometer. The PL spectra were obtained by excitation at the absorption maxima and recorded with an ISA SPEX Triax 180 spectrograph coupled to a Spectrum-1 liquid nitrogen-cooled charge coupled device
(CCD) detector. This part of work was done by Richard Farley in Dr. Kirk Schanze group in the Department of Chemistry at the University of Florida.

Figure 4-1. Molecular structures and photoluminescence spectra of two near-IR emitting donor-acceptor-donor oligomers, BEDOT-TQMe$_2$ and BEDOT-BBT, in CH$_2$Cl$_2$ solutions. (courtesy of Richard Farley)

NIR OLED devices were fabricated via vacuum thermal evaporation on glass substrates commercially pre-coated with an indium tin oxide (ITO) anode (sheet resistance ~ 20 Ω/☐). The substrates were cleaned in ultrasonic baths of deionized water, acetone, and isopropanol consecutively for 15 minutes each, and were then exposed to an ultraviolet ozone ambient for 15 minutes immediately before loading into a high vacuum chamber (base pressure ~ 10$^{-7}$ Torr). To fabricate a fluorescent OLED, a 40 nm thick hole transporting layer (HTL) of bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl (α-NPD), a 20 nm thick emissive layer (EML) consisting of an Alq$_3$ host doped with either NIR emitter, an electron transport layer (ETL) of bathocuproine (BCP), and a 1 nm thick LiF layer followed an Al cathode layer (50 nm thick) were successively
deposited on the substrates. The doping concentration of the NIR emitters in the EML was varied from 0% to 5% by weight, whereas the thickness of the BCP ETL was varied from 40 nm to 110 nm.

For the sensitized fluorescent devices, 4,4′-bis(carbazol-9-yl)biphenyl (CBP) was used as the host material in the EML, which also incorporates a phosphorescent sensitizer in addition to the NIR emitters. tris(2-phenylpyridine)iridium(III) (Ir(ppy)₃) and bis(2-phenylquinoxaline)(acetylacetonate)iridium(III) (PQIr) were used as the phosphorescent sensitizers, both with 10 wt.% doping concentration, for BEDOT-TQMe₂ and BEDOT-BBT based devices, respectively.

The deposition rates for the organic layers were 0.1-0.2 nm/s, as monitored by quartz crystal microbalances. The active device area was 4 mm² with the electrodes arranged in a cross-bar geometry, and each substrate featured four independently addressable device pixels. Ir(ppy)₃ and PQIr were purchased from Luminescence Technology Corp., Alq₃ and BCP from TCI America, α-NPD from e-Ray, and CBP from Springchem & Jadetextile Group Ltd. All organic materials were used as obtained except for α-NPD and Alq₃, which were purified in house using vacuum gradient sublimation method for one to two cycles.

Radiant emittance (R) – current density (J) – voltage (V) characteristics of the NIR OLEDs were measured in ambient using an Agilent 4155C semiconductor parameter analyzer and a calibrated silicon detector (Newport 818 UV). EL spectra were taken with the ISA SPEX Triax 180 spectrograph with the devices driven at a constant current using a Keithley 2400 source meter. The radiant emittance was calibrated assuming Lambertian emission, and the EQE (\(\eta_{EQE}\)) and “wall plug” power efficiency (\(\eta_P\)) were
derived based on the recommended methods. The organic layer thickness non-uniformity across the samples and run-to-run variations typically lead to 5-10% error in device efficiencies.

4.4 Near-Infrared OLEDs based on DAD oligomers

4.4.1. Optical Properties of the DAD Oligomers

The absorption spectra of the two DAD molecules in CH$_2$Cl$_2$ solutions are shown in Figure 4-2. BEDOT-TQMe$_2$ features a strong absorption peak at 370 nm and also a longer wavelength absorption peak at $\lambda = 531$ nm. The absorption of BEDOT-BBT in the 350-400 nm range is similar to that of BEDOT-TQMe$_2$; however, the longer wavelength absorption band is red-shifted by 120 nm, to $\lambda = 650$ nm, due to the stronger electron acceptor component in BEDOT-BBT, which leads to a lower lying LUMO level and thus a lower HOMO-LUMO energy band gap. The PL spectrum of Alq$_3$ host is also shown in Figure 4-2 for comparison.

![Figure 4-2. (color) Absorption spectra of BEDOT-TQMe$_2$ (red) and BEDOT-BBT (blue) in CH$_2$Cl$_2$ solutions. The photoluminescence spectrum of Alq$_3$ is also shown by green dashed line.](image-url)
Accordingly, compared to the PL band of BEDOT-TQMe$_2$ which has a maximum wavelength at $\lambda = 698$ nm, the PL of BEDOT-BBT is also red-shifted by more than 100 nm, to a maximum wavelength at $\lambda = 805$ nm, as shown in Figure 4-1. The PL quantum yield for BEDOT-TQMe$_2$ is measured to be 21%, whereas that for BEDOT-BBT is three times lower, only 7.6%. The lower quantum yield of the latter molecule is at least in part due to the increased non-radiative decay rate in this lower band gap molecule. From the absorption and PL spectra, the HOMO-LUMO gaps of BEDOT-TQMe$_2$ and BEDOT-BBT are determined to be approximately 2.0 and 1.6 eV, respectively.

4.4.2. Fluorescent NIR OLEDs based on the DAD Oligomers

The electroluminescence spectra of OLEDs with various doping concentrations of BEDOT-TQMe$_2$ in the Alq$_3$ host matrix and the schematic energy level diagram of these devices are shown in Figure 4-3A. The electrode work functions and the HOMO/LUMO energies for $\alpha$-NPD, Alq$_3$, and BCP are taken from the literature,$^{159,160}$ whereas the HOMO/LUMO energies for the NIR emitters are estimated from a combination of solution cyclic voltammetry, differential pulse voltammetry, and spectroscopic measurements. The BCP thickness in these devices is maintained at 50 nm.

In Figure 4-3A, the undoped device (0% doping) shows an emission peak at $\lambda = 518$ nm, which is solely from the Alq$_3$ host molecules. With BEDOT-TQMe$_2$ doped into Alq$_3$, the Alq$_3$ host emission is quenched and emission from the dopant molecules is observed. The peak emission wavelengths of the doped devices are at $\lambda = 690$-698 nm, slightly blue shifted compared to the PL peak of BEDOT-TQMe$_2$ in solution, but red-shifted significantly from the emission of the Alq$_3$ host. Efficient Förster energy transfer$^{114}$ occurs from Alq$_3$ to BEDOT-TQMe$_2$ molecules, as the emission spectrum of Alq$_3$ almost completely overlaps with the absorption spectrum of BEDOT-TQMe$_2$, as
Figure 4-3. (color) A) Normalized electroluminescence (EL) spectra of OLEDs with various BEDOT-TQMe₂ doping concentration in the emissive layer: 0% (green solid lines), 2% (red dash-dotted lines), and 5% (blue dashed lines). The BCP layer thickness is 50 nm. Inset: The schematic energy level diagram of the OLEDs. The energies (in eV) are measured from the vacuum level. The upper dashed line and the dash-dotted line in the Alq₃ layer correspond to the LUMOs for BEDOT-TQMe₂ and BEDOT-BBT, respectively, whereas the lower dashed lines correspond to the HOMO of both molecules. B) External quantum efficiency, $\eta_{EQE}$, and power efficiency, $\eta_P$, as functions of current density, $J$, for these OLEDs.

shown in Figure 4-2. The intensity of the original Alq₃ emission is less than 1% of that of the NIR peak for the 2% doped device. The Alq₃ emission completely disappears when the BEDOT-TQMe₂ doping concentration is increased to 5%; however, this leads to a considerable decrease of the EQE, due to aggregate quenching, from a maximum of
0.91% for the 2% doped device to 0.74% for the 5% doped device, as shown in Figure 4-3B. Similarly, the power efficiency is also decreased from a maximum of 5.4 mW/W for the 2% doped device to 3.9 mW/W for the 5% doped device. Therefore in subsequent work, we employed a 3.5% BEDOT-TQMe₂ doping concentration to achieve a proper balance between the maximum energy transfer and minimum concentration quenching.

Figure 4-4. (color) A) External quantum efficiency, $\eta_{\text{EQE}}$, of OLEDs with various BCP ETL thickness (with 3.5% BEDOT-TQMe₂ doping concentration in the emissive layer), as functions of current density, $J$. B) Maximum $\eta_{\text{EQE}}$ (solid) and $\eta_{\text{EQE}}$ at $J = 1 \text{ mA/cm}^2$ (open) of these OLEDs as functions of the BCP layer thickness, $t_{\text{BCP}}$.

With a constant 3.5% BEDOT-TQMe₂ doping concentration in Alq₃, the thickness of the BCP ETL, $t_{\text{BCP}}$, was varied from 40 nm to 100 nm. Figure 4-4A shows the EQEs of these devices change as the varied BCP ETL thickness. The maximum EQE as well as the efficiencies at $J = 1 \text{ mA/cm}^2$, are summarized in Figure 4-4B. Both efficiency curves show the same trend, i.e. the efficiencies increase with $t_{\text{BCP}}$ for 40 nm < $t_{\text{BCP}}$ < 80 nm, and then decrease with further increase in $t_{\text{BCP}}$ to 100 nm. With an 80 nm thick BCP ETL, a maximum EQE of $\eta_{\text{EQE}} = (1.6 \pm 0.2)\%$ is achieved.
The optimal ETL thickness here is much greater than that usually used in OLEDs emitting visible light. This can be attributed to the weak microcavity effect existing in the OLED device structure, as the emission zone needs to be located approximately at a distance of $\lambda/4n$ away from the reflecting electrode (cathode) to maximize the coupling of the emission into the external modes. Here, $\lambda$ is the emission wavelength, and $n$ ($\approx 1.5-2.0$) is the refractive index of the organic materials. Therefore, the longer wavelengths of NIR emission, compared to visible emission, require a thicker ETL to achieve the optimized performance. The thicker ETL, however, does lead to higher operating voltages for the OLEDs. Overall, when $t_{BCP}$ is increased from 40 nm to 80 nm, both the maximum $\eta_{EQE}$ and $\eta_{EQE}$ at $J = 1 \text{ mA/cm}^2$ are increased by a factor of 2.5, whereas the maximum $\eta_P$ is only increased by 80%, and the enhancement in $\eta_P$ at $J = 1 \text{ mA/cm}^2$ is even smaller, only 30%, due to the significant increase in operating voltage.

Figure 4-5. (color) External quantum efficiency, $\eta_{EQE}$ as a function of current density, $J$, for OLEDs (with 3.5% BEDOT-BBT doping concentration in the emissive layer) with different BCP ETL layer thickness: 50 nm (solid green squares), 80 nm (open black circles), 100 nm (open red triangles), and 110 nm (solid blue diamonds).
We have also studied the effect of doping concentration and ETL thickness on the efficiencies of BEDOT-BBT based NIR OLEDs. The optimal doping concentration of BEDOT-BBT is found to be 3.5%, the same as BEDOT-TQMe₂. Figure 4-5 shows the EQE for BEDOT-BBT based NIR OLEDs with different BCP layer thickness, which was varied from 50 nm to 110 nm. By comparing the EQE of devices with different BCP thickness, the optimal BCP thickness is found to be 100 nm, slightly thicker than that in the optimal BEDOT-TQMe₂ based devices, consistent with the longer wavelength emission of the BEDOT-BBT (Figure 4-1) according to the microcavity effect.

![Normalized EL spectra and current density and radiant emittance](image)

Figure 4-6. A) Normalized electroluminescence (EL) spectra, for optimal fluorescent (NF) OLEDs based on BEDOT-TQMe₂ (dashed line) and BEDOT-BBT (solid line). B) Current density $J$ and the radiant emittance in the forward viewing direction $R$ as functions of the voltage $V$ for these two optimal OLEDs.
As shown in Figure 4-6A, with 3.5% BEDOT-BBT doped into Alq₃, the host emission is barely apparent with an intensity of approximately 3% of that of the NIR peak at 815 nm, compared to the nearly complete quenching of host emission in the BEDOT-TQMe₂ based device with the same doping concentration. Increasing the BEDOT-BBT doping concentration to over 5% could completely remove the Alq₃ emission as well; however, this also leads to a decrease in the EQE by more than 25%, again due to aggregate quenching.¹⁶¹ The higher doping concentration of BEDOT-BBT needed to completely quench the host emission, compared to BEDOT-TQMe₂, is consistent with the extent of overlap between the emission spectrum of the Alq₃ host (Figure 4-2) and the absorption spectra of the two NIR emitters. As shown in Figure 4-2, BEDOT-TQMe₂ has an absorption peak at λ = 531 nm, which overlaps with the emission from Alq₃ very significantly. However, for the BEDOT-BBT molecule, the absorption peak is red-shifted to λ = 650 nm, leading to a much less overlap with the Alq₃ emission spectrum. As the Förster energy transfer radius from the host to guest is determined by such spectral overlap,¹¹⁴ this means that the Förster radius is smaller for energy transfer from Alq₃ to BEDOT-BBT compared to that for Alq₃ to BEDOT-TQMe₂, and therefore a higher concentration of BEDOT-BBT is needed to allow complete energy transfer for excitons on Alq₃ host molecules. Based on the methods previously reported,¹²⁹,¹⁶²,¹⁶³ the Förster radii for energy transfer from Alq₃ to BEDOT-TQMe₂ and BEDOT-BBT are 28 and 22 Å, respectively, which are consistent with what we expect.

Another host material with more spectral overlap could then be used to replace Alq₃ to improve the Förster energy transfer in the BEDOT-BBT devices. Alternatively, cascaded energy transfer¹⁶⁴ from the host to an intermediate molecule and then to the
NIR emitter could also be used. This will be important when NIR emitters with even longer wavelength emissions are to be used.

The $R$-$J$-$V$ characteristics for the BEDOT-TQMe$_2$ and BEDOT-BBT based fluorescent NIR OLEDs with 3.5 wt% doping concentrations in the EML and the optimal ETL thicknesses are shown in Figure 4-6B. The BEDOT-BBT based device has slightly higher turn-on voltage and lower current density than the BEDOT-TQMe$_2$ based device, due to the slightly thicker BCP ETL of in the former device (100 nm vs. 80 nm). Maximum radiant emittances of $R = 6$ and 0.5 mW/cm$^2$ are achieved for BEDOT-TQMe$_2$ and BEDOT-BBT based fluorescent devices, respectively, at $V = 20$ V.

Figure 4-7 shows the dependencies of $\eta_{EQE}$ and $\eta_P$ on the current density for BEDOT-TQMe$_2$ and BEDOT-BBT based fluorescent OLEDs (labeled as “NF”) with 3.5 wt% doping concentrations in the EML and the optimal ETL thicknesses. The BEDOT-TQMe$_2$ based device has a maximum EQE of $\eta_{EQE} = (1.6 \pm 0.2)\%$ achieved at $J \approx 10^{-2}$ mA/cm$^2$, slowly decreasing to $\eta_{EQE} = 0.7\%$ at $J = 400$ mA/cm$^2$. The EQE for the BEDOT-BBT based device is lower, with a maximum of $\eta_{EQE} = (0.51 \pm 0.05)\%$ achieved at $10^{-3}$ mA/cm$^2 < J < 10^{-2}$ mA/cm$^2$, although its roll-off at higher current densities is less significant and it remains above 0.35%, or 70% of the maximum value, for $J$ up to 100 mA/cm$^2$. The maximum EQE of these two devices are approximately proportional to the corresponding fluorescent quantum yields of the DAD oligomers.

The power efficiency is also higher for the BEDOT-TQMe$_2$ based device than the BEDOT-BBT based device, with a maximum of $\eta_P = (7.0 \pm 0.7)$ mW/W for the former device and $(2.1 \pm 0.2)$ mW/W for the latter, both achieved at low current densities ($J < 10^{-3}$ mA/cm$^2$). The lower power efficiency in the latter device is mainly due to the lower
EQE (0.5% vs. 1.6%), but is also affected by the slightly higher operating voltage (thicker BCP ETL) and the longer emission wavelength (thus lower photon energy) for BEDOT-BBT compared with BEDOT-TQMe₂ (Figure 4-1).

Figure 4-7. (color) External quantum efficiency, $\eta_{\text{EQE}}$, and power efficiency, $\eta_P$, as functions of current density, $J$, for fluorescent (NF) and sensitized fluorescent (SF) OLEDs based on: A) BEDOT-TQMe₂, and B) BEDOT-BBT.

4.4.3. Sensitized Fluorescent NIR OLEDs based on the DAD Oligomers

The energy transfer mechanism of the above fluorescent NIR OLEDs can be summarized by the schematics shown in Figure 4-8A. Both singlet (S) and triplet (T) excitons are formed in the host molecules with a ratio of 1:3 according to spin
statistics\textsuperscript{165} But only the singlet excitons in the host molecules are transferred to the NIR emitting molecules through the Förster energy transfer process, from which fluorescent emissions are achieved. However, the triplet excitons formed on the host molecules, which are three times more in number than the singlet excitons, are non-radiatively recombined and not harvested at all, due to the requirement of spin-symmetry conservation for these fluorescent molecules.

Figure 4-8. (color) Energy transfer mechanisms in: A) normal fluorescence (NF), and B) sensitized fluorescence (SF) systems. Förster energy transfers are represented by solid black lines and Dexter energy transfers by dashed black lines. Intersystem crossing (ISC) is represented by solid green line. Dashed red lines indicate that certain processes have no contribution to the device emission and result in a loss in efficiency.

To harvest both singlet and triplet excitons in OLEDs with fluorescent emitters, the so-called “sensitized fluorescence” device architecture has been demonstrated, in which a phosphorescent dye is incorporated in the emissive layer together with the host and fluorescent molecules to funnel the triplet excitons formed on the host molecules to the fluorescent emitters, or “sensitize” the fluorescent molecules\textsuperscript{154} Theoretically, all the excitons now can be converted to singlet excitons on fluorescent dyes. This mechanism of sensitized fluorescence is shown in Figure 4-8B. So ideally, by applying the
sensitized fluorescence to the devices, the efficiencies can be increased by three times compared to the normal fluorescent devices. But in fact, the real enhancement factors will usually be lower due to several loss mechanisms involved in the sensitized fluorescence system, shown by the dashed red lines in Figure 4-8B. There is a probable source of loss of direct transfer from the triplet states of host molecules into the triplet states of the fluorescent dye by a Dexter transfer, which is very similar to what happens in normal fluorescence system. Furthermore, singlet excitons in the phosphorescent sensitizer are subject to intersystem crossing (ISC) and transfer to the triplet states, from which triplet excitons may Dexter energy transfer to the triplet states of fluorescent dye. This is another loss mechanism. Finally, direct formation of triplets on the fluorescent dye is an additional path to loss (not shown in the figure). Overall, all these loss paths will result in a less enhancement than that expected by ideal situation in the sensitized fluorescent devices.

Here, we use two molecules, Ir(ppy)$_3$ and PQIr$^{49,154,156,157}$ as the phosphorescent sensitizers for BEDOT-TQMe$_2$ and BEDOT-BBT, respectively, and CBP is used as the host instead of Alq$_3$. The doping concentration of both phosphorescent sensitizers is 10% by weight. BEDOT-TQMe$_2$ doping concentration is slightly decreased from 3.5% to 3%, whereas that of BEDOT-BBT is maintained at 3.5%. The BCP ETL thicknesses are the same as in the optimized fluorescent devices (80 nm for BEDOT-TQMe$_2$ and 100 nm for BEDOT-BBT).

The $J$-$V$ characteristics of these two sensitized fluorescent NIR OLEDs are shown in Figure 4-9. Compared to the fluorescent devices exhibiting turn-on voltages of 2.7 V, the two sensitized fluorescent devices have slightly higher turn-on voltages of 3.4 V,
probably due to the charge trapping behavior of the phosphorescent sensitizers. At high voltages ($V > 5$ V for BEDOT-TQMe$_2$ and $V > 11$ V for BEDOT-BBT), the sensitized fluorescent devices show higher current densities than the corresponding fluorescent devices. This could be attributed to the higher electron mobility of the CBP host in the sensitized fluorescent devices than that of the Alq$_3$ host in the fluorescent devices. The radiant emittances in the forward-viewing direction of the devices are also shown in Figure 4-9. The devices with sensitized fluorescence, as expected, have higher radiant emittances than their corresponding fluorescent devices. The maximum radiant emittances for BEDOT-TQMe$_2$ and BEDOT-BBT based sensitized fluorescent devices are $R = 19$ and $2$ mW/cm$^2$, respectively, achieved at $V = 20$ V, which are more than three times higher than those of the corresponding fluorescent devices.

![Graph showing current density, $J$, and the radiant emittance in the forward viewing directions, $R$, as functions of the voltage, $V$, for sensitized fluorescent (SF) OLEDs based on BEDOT-TQMe$_2$ and BEDOT-BBT.](image)

Figure 4-9. Current density, $J$, and the radiant emittance in the forward viewing directions, $R$, as functions of the voltage, $V$, for sensitized fluorescent (SF) OLEDs based on BEDOT-TQMe$_2$ and BEDOT-BBT.

The EQE and power efficiencies of the sensitized fluorescent devices (labeled as “SF”) as compared to those of the optimized fluorescent devices are shown in Figure 4-7. The EQE of the BEDOT-TQMe$_2$ based sensitized fluorescent device reaches a
maximum of $\eta_{EQE} = (3.1 \pm 0.3)\%$ at $J \approx 10^{-2} \text{ mA/cm}^2$, and slowly decreases with increasing current density, but still achieves $\eta_{EQE} = 1.6\%$ at $J \approx 100 \text{ mA/cm}^2$. For the BEDOT-BBT based sensitized fluorescent device, the maximum EQE is $\eta_{EQE} = (1.5 \pm 0.2)\%$, also achieved at $J \approx 10^{-2} \text{ mA/cm}^2$, and its slow roll-off at higher current densities is similar to the corresponding fluorescent device. Hence, using the sensitized fluorescent device structure, we have achieved a two and three times higher EQE for the BEDOT-TQMe$_2$ and BEDOT-BBT based NIR OLEDs, respectively. These enhancement, which are lower than the theoretical value in the ideal situation, result from several possible loss mechanisms involved in the sensitized fluorescence system, as we discussed above (Figure 4-8). The maximum power efficiency is $\eta_P = (12 \pm 2)$ mW/W for the BEDOT-TQMe$_2$ based sensitized fluorescent device, and is $(4.0 \pm 0.4)$ mW/W for the BEDOT-BBT based device, both approximately twice of that achieved in the normal fluorescent devices.

![Figure 4-10](image-url)

Figure 4-10. (color) Normalized electroluminescence (EL) spectra, for sensitized fluorescent (SF) OLEDs based on BEDOT-TQMe$_2$ and BEDOT-BBT. The EL spectra for the two fluorescent (NF) OLEDs are also shown for comparison.
Figure 4-10 shows the EL spectra of the sensitized fluorescent NIR OLEDs based on BEDOT-TQMe$_2$ and BEDOT-BBT. For comparison, the EL spectra of the two fluorescent devices are also shown. The peak emission wavelength for BEDOT-TQMe$_2$ based sensitized fluorescent devices is at $\lambda = 692$ nm, whereas that for BEDOT-BBT based sensitized fluorescent devices is at $\lambda = 815$ nm, both of which are nearly identical to the corresponding fluorescent devices. However, unlike the fluorescent devices in which the host emission is almost completely quenched, the two sensitized fluorescent devices still show appreciable emissions (10-15%) from the phosphorescent sensitizers, with the emission peak at around 510 nm from Ir(ppy)$_3$ and that at 583 nm from PQIr.$^{49,154,156,157}$ This suggests an incomplete energy transfer of the triplet excitons from the phosphorescent sensitizers to the NIR fluorescent emitters, similar to that has been observed previously.$^{154}$

![Normalized electroluminescence spectra for BEDOT-TQMe$_2$ based sensitized fluorescence OLEDs with different doping concentration of near-IR fluorescent emitter. External quantum efficiency, $\eta_{EQE}$, as a function of the current density, $J$, for these devices.](image)

Figure 4-11. (color) A) Normalized electroluminescence spectra for BEDOT-TQMe$_2$ based sensitized fluorescence OLEDs with different doping concentration of near-IR fluorescent emitter. B) External quantum efficiency, $\eta_{EQE}$, as a function of the current density, $J$, for these devices.

More complete energy transfer could be induced with higher concentrations of the fluorescent emitter in the emissive layer. As shown in the Figure 4-11A, as the BEDOT-
TQMe$_2$ concentration increases from 3% to 5%, the intensity of the Ir(ppy)$_3$ emission is nearly completely suppressed. The EQE of this SF device, however, is also reduced as shown in Figure 4-11B. While a maximum EQE of $\eta_{EQE} = 3.1\%$ is achieved for a 3% BEDOT-TQMe$_2$ doping concentration, a maximum EQE of only 1.6% is obtained for the device with a 5% BEDOT-TQMe$_2$ doping concentration, which again is attributed to aggregation induced fluorescence quenching.$^{161}$

![Figure 4-12. (color) A) Normalized electroluminescence spectra for BEDOT-BBT based sensitized fluorescence OLEDs with different doping concentration of the phosphorescent sensitizer, PQIr. B) External quantum efficiency, $\eta_{EQE}$, as a function of the current density, $J$, for these devices.](image)

The concentration of the phosphorescent sensitizer also affects the energy transfer, although the effect is less prominent. As shown in Figure 4-12A, when the PQIr concentration in the BEDOT-BBT based SF device is increased from 10% to 15%, the PQIr emission is slightly reduced. Accordingly, the maximum EQE of the device is also slightly reduced from $\eta_{EQE} = 1.5\%$ to 1.4%, as shown in Figure 4-12B.

4.5 Aggregation of Donor-Acceptor-Donor Moleclues

Previously, we have studied the NIR OLEDs with different doping concentration based on BEDOT-TQMe$_2$ and BEDOT-BBT (Figure 4-3). It is found that when low
doping concentration (2%) is used in the emissive layer with Alq₃ host molecules, the Alq₃ emission cannot be completely quenched for both BEDOT-TQMe₂ and BEDOT-BBT based devices, due to the incomplete energy transfer between the host and guest molecules. Further increasing the doping concentration will help solve this problem. As shown in Figure 4-3, the Alq₃ emission completely disappears when the BEDOT-TQMe₂ doping concentration is increased to 5%; however, this leads to a considerable decrease of the EQE and power efficiency, due to aggregate quenching.¹⁶¹

![Figure 4-13. (color) The spectral overlaps between absorption spectra of BEDOT-BBT (blue solid) in CH₂Cl₂ solutions and emission spectrum of Alq₃ (green dashed) and CBP (red dashed).](image)

For BEDOT-BBT, the doping concentration needs to be increase to over 5% to completely quench the emission from Alq₃, because the absorption of BEDOT-BBT has a much less overlap with the Alq₃ emission spectrum compared to BEDOT-TQMe₂ (Figure 4-2). As the Förster energy transfer radius from the host to guest is determined by such spectral overlap,¹¹⁴ this means that the Förster radius is smaller for energy transfer from Alq₃ to BEDOT-BBT compared to that for Alq₃ to BEDOT-TQMe₂, and therefore a higher concentration of BEDOT-BBT is needed to allow complete energy
transfer for excitons on the Alq₃ host molecules. So in that case, the aggregate quenching issue will be more significant for BEDOT-BBT. In previous work, we employed a 3.5% doping concentration for both BEDOT-TQMe₂ and BEDOT-BBT based near-IR OLEDs, to achieve a compromise between the maximum energy transfer and minimum aggregate quenching, although the near-IR OLEDs based on both molecules still show small amount intensity of Alq₃ emission.

Figure 4-14. Molecular structures of two near infrared-emitting bulky donor-acceptor-donor oligomers. The molecular structure of BEDOT-BBT is also shown for comparison.

But, as the NIR emitters with even longer emission wavelength were used, methods have to be found out to better address these issues. One way is to use another host material to replace Alq₃ to increase the spectral overlap with the NIR emitters, by which the concentration of NIR emitters needed to allow complete energy transfer for excitons on the host molecules will be decreased due to increased Förster radius. Then the aggregate quenching issue will be less significant. Another way is to
change the stacking manner of emitter molecules and thus manipulate the inter-
molecular interaction and aggregation.

Here, we replace the host material of Al$_3$ with CBP, which has more spectral
overlap$^{168}$ with the longer emission near-IR emitter, BEDOT-BBT, as shown in Figure 4-13. Instead of very limited overlapping with the absorption peak at $\lambda = 650$ nm for Al$_3$ host, CBP host will have more spectral overlap with the shorter absorption peak of BEDOT-BBT at $\lambda = 350$ nm. Furthermore, to decrease the aggregation between molecules, we add two different types of bulky end groups to the two sides of the DAD oligomers, called bulky DAD oligomers. The molecular structures of these two bulky DAD oligomers, Bu$_3$Si-Th-BBT and EtHx-Th-BBT, are shown in Figure 4-14. Compared to the structure of BEDOT-BBT, which is also shown in Figure 4-14, the two types of bulky end groups in the bulky DAD oligomers are designed to reduce the aggregation between molecules.

Figure 4-15A shows the EL spectra comparison of the NIR OLEDs based on
BEDOT-BBT with different host materials. The doping concentration of BEDOT-BBT is 3.5% and BCP thickness is 100 nm for both devices. The host emission, which is supposed to be peaked at 420 nm, is nearly completely quenched in the devices using CBP as host, while the devices with Al$_3$ as host still show approximately 3% of the intensity of the NIR peak at 815 nm. This is mainly due to the larger spectral overlap of CBP with BEDOT-BBT than Al$_3$, which leads to more complete Förster energy transfer between host and guest. The two devices show similar turn-on voltages but the devices with CBP show higher current densities than the devices with Al$_3$ as shown in Figure 4-15B. This could be attributed to the higher electron mobility of the CBP host than that of
Figure 4-15. (color) A) Normalized electroluminescence (EL) spectra of NIR OLEDs based on BEDOT-BBT using CBP (black dashed lines) and Alq₃ (red solid lines) as host material (with 3.5% doping concentration of BEDOT-BBT). B) Current density, \( J \), and radiant emittance in the forward viewing directions, \( R \), as functions of voltage, \( V \), for the two OLEDs with different hosts: CBP (black squares) and Alq₃ (red triangles). C) External quantum efficiency, \( \eta_{EQE} \), and power efficiency, \( \eta_p \), as functions of current density, \( J \), for the two OLEDs with different hosts: CBP (black squares) and Alq₃ (red triangles).
the Alq3 host. The radiant emittances in the forward-viewing direction of these two devices are also compared in Figure 4-15B. The devices with CBP host, as expected, have higher radiant emittances than the devices with Alq3 host. The maximum radiant emittance for the devices with CBP host is \( R = 5.5 \text{ mW/cm}^2 \) achieved at \( V = 15 \text{ V} \), which is more than ten times higher than that of the devices with Alq3 host.

Figure 4-15C shows the dependencies of \( \eta_{EQE} \) and \( \eta_P \) on the current density for these two NIR OLEDs. The device with CBP host has a maximum EQE of \( \eta_{EQE} = (0.92 \pm 0.07)\% \) achieved at \( J \approx 10^{-1} \text{ mA/cm}^2 \), which is almost double that of the devices with Alq3 as host. The power efficiency is also higher for the CBP device than the device with Alq3 host, with a maximum of \( \eta_P = (3.6 \pm 0.3) \text{ mW/W} \) for the former device, achieved at current densities of \( J \approx 10^{-2} \text{ mA/cm}^2 \).

![Figure 4-16](image)

Figure 4-16. (color) External quantum efficiency, \( \eta_{EQE} \) of OLEDs based on three DAD oligomers (BEDOT-BBT: black squares, Bu3Si-Th-BBT: red triangles, EtHx-Th-BBT: blue circles) as a function of doping concentration, \( x \) (\( x = 2\%, 4\%, 7\% \) and \( 10\% \)), of these NIR emitters. Solid and open symbols are for maximum EQE and EQE at a current density of \( 10 \text{ mA/cm}^2 \), respectively.
We apply the same device structure which uses CBP as host material to the NIR OLEDs based on Bu₃Si-Th-BBT and EtHx-Th-BBT. To study the aggregation of the DAD oligomers in the devices, the doping concentration of the DAD oligomers in the OLEDs was varied from 2% to 10%. The maximum EQE as well as the efficiency at \( J = 10 \text{ mA/cm}^2 \) are summarized in Figure 4-16. The corresponding device results of NIR OLEDs based on BEDOT-BBT are also shown for comparison.

All six efficiency curves show the same trend that the EQE of these OLEDs gradually decreases with the increasing doping concentration of DAD oligomers, which can be attributed to the aggregate quenching as we have mentioned above. The decrease rate, which can be indicated by the slope of the efficiency curve, represents the extent of aggregation of the DAD oligomers in the devices. The NIR OLEDs based on EtHx-Th-BBT have similar efficiency decrease rate as the BEDOT-BBT based OLEDs, while the decrease rate for the Bu₃Si-Th-BBT based OLEDs is slightly higher. This means Bu₃Si-Th-BBT and EtHx-Th-BBT have similar aggregation in the OLEDs as the BEDOT-BBT based OLEDs have. This result is surprise to us as the bulky groups in the two sides of the DAD oligomers actually did not reduce the aggregation between molecules as we have expected. The EQE of the NIR OLEDs based on EtHx-Th-BBT is much lower than that of the BEDOT-BBT based OLEDs at all doping concentrations, while the Bu₃Si-Th-BBT based OLEDs shows close EQE to the BEDOT-BBT based OLEDs at 4% and 7% doping concentration, and 30% lower EQE when doping concentration increases to 10%.

The EL emission of NIR OLEDs based on Bu₃Si-Th-BBT with 4% doping concentration is moved to longer wavelength with peak at 865 nm as shown in Figure 4-
17, while the efficiency still keeps the same, compare to the BEDOT-BBT devices. NIR OLEDs based on EtHx-Th-BBT show even longer emission peaked at 905 nm, although the EQE is much lower than that of BEDOT-BBT based OLEDs (Figure 4-16). The OLEDs based on Bu$_3$Si-Th-BBT and EtHx-Th-BBT both show small amount intensity of host emission at wavelength of 420 nm, due to incomplete energy transfer. Different from BEDOT-BBT based device which only show one single peak in the near-IR range, the OLEDs based on these two bulky DAD oligomers also exhibit a similar secondary peak at $\lambda = 730$-$740$ nm with an intensity of approximately 25% of that of the near-IR peaks. This can be probably attributed to the decomposition of the two bulky DAD oligomers that the chemical bonds connecting the bulky end groups and DAD macrocycle rings break down.

![EL spectrum graph](image)

Figure 4-17. (color) Normalized electroluminescence (EL) spectra of NIR OLEDs based on three DAD oligomers: BEDOT-BBT (black dashed lines), Bu$_3$Si-Th-BBT (red solid lines), EtHx-Th-BBT (blue dotted lines). The doping concentration is 4% for all devices with CBP as host in the emissive layer.

### 4.6 Summary

In this chapter, we demonstrate here that low-gap DAD oligomers are good candidate materials for use in OLEDs to achieve efficient NIR emission. A maximum
external quantum efficiency of 1.6% and a maximum power efficiency of 7.0 mW/W were achieved in devices based on BEDOT-TQMe$_2$, whose emission peaks at 692 nm, but extends to well above 800 nm. With a stronger acceptor and thus a reduced energy gap, longer wavelength NIR emissions peaked at 815 nm were achieved in BEDOT-BBT based devices, although the efficiencies were approximately three times lower than the BEDOT-TQMe$_2$ based devices, due to the significantly lower fluorescent quantum yield of BEDOT-BBT. Using the sensitized fluorescence device structure, the efficiencies were further increased by two to three times, and we achieved the maximum efficiencies of $\eta_{EQE} = 3.1\%$ and $\eta_P = 12$ mW/W for BEDOT-TQMe$_2$ based devices, and $\eta_{EQE} = 1.5\%$ and $\eta_P = 4.0$ mW/W for BEDOT-BBT based devices.

The aggregate effect of the donor-acceptor-donor oligomers in the devices is also studied by utilizing different host matrix and changing the stacking manners of doping molecules. Changing from the previous host of Alq$_3$ to CBP, which has more spectral overlap with the DAD NIR emitters, the concentration of NIR emitters needed to allow complete energy transfer for excitons on the host molecules will be decreased due to increased Förster radius, leading to less significant aggregate quenching effect. The NIR OLEDs based on BEDOT-BBT doped into CBP host matrix has a maximum EQE of $\eta_{EQE} = (0.92 \pm 0.07)\%$, which is almost double that of the devices with Alq$_3$ as host. The power efficiency is also higher for the CBP device than the device with Alq$_3$ host, with a maximum of $\eta_P = (3.6 \pm 0.3)$ mW/W for the former device. The effect of molecular structure on aggregation in devices is then studied by adding bulky substituted groups to the two ends of DAD oligomers. However, the NIR OLEDs based on two bulky DAD oligomers show similar aggregate effect, compared to “bare” BEDOT-BBT based
devices. The efficiencies of these bulky DAD oligomers based devices show no enhancement and the emissions are red-shifted with peak emission wavelengths up to 905 nm.
CHAPTER 5
NEAR-INFRARED ORGANIC LIGHT-EMITTING DEVICES BASED ON PHOSPHORESCENT PLATINUM (II) PORPHYRINS

5.1 Introduction

In last chapter, the fluorescent donor-acceptor-donor oligomers featuring tunable emission from 700-900 nm have been integrated into OLEDs with device efficiencies in the 1% to 3% range for devices emitting between 700-860 nm, but dropping below 0.5% for devices emitting above 900 nm. A major shortcoming of the oligomers and other fluorescent materials is that they only emit from the singlet state, which limits the electroluminescent internal quantum efficiencies achievable to approximately 25%. The triplet excitons, which are three times more in number than the singlet excitons, are not harvested at all, due to the requirement of spin-symmetry conservation for these fluorescent molecules. To harvest both singlet and triplet excitons in OLEDs with fluorescent emitters, the so-called “sensitized fluorescence” device architecture has been used, in which a phosphorescent dye is incorporated in the emissive layer together with the host and fluorescent molecules to funnel the triplet excitons formed on the host molecules to the fluorescent emitters, or “sensitize” the fluorescent molecules. But there still exists several loss mechanisms of triplet excitons, leading to less enhancement than that expected by ideal situation. Additionally, the solution quantum yields of near-IR emitting donor-acceptor-donor oligomers are usually low ($\phi_{em} < 0.25$), which also results in the low efficiencies for the OLEDs. So it is necessary to develop the real phosphorescent near-IR emitters, by which 100% internal quantum efficiency can be achieved, for the higher efficiencies of the near-IR OLEDs.

Phosphorescent metal-organic complexes provide attractive candidates for use in PLEDs and OLEDs due, in part, to their high luminescence quantum yields and nearly
100% internal quantum efficiencies due to their ability to efficiently emit from the spin-orbit mixed triplet states.\textsuperscript{34,35} Previously, two classes of phosphorescent metal-organic complexes have been employed as dopants in NIR OLEDs. The first utilized trivalent lanthanide cations (Ln\textsuperscript{3+}) as the emitting centers, for example, Er\textsuperscript{3+} or Nd\textsuperscript{3+}, chelated with chromophoric ligands to sensitize excitation-energy transfer to the lanthanide ion.\textsuperscript{169} Schanze et al. have reported a near-IR OLED utilizing Ln\textsuperscript{3+} in conjugation with a porphyrin/polystyrene matrix, with EQE ranging from 8.0×10^{-4} to 2.0×10^{-4}\% at approximately 1 mA/cm\textsuperscript{2}.\textsuperscript{68} Similarly, a Nd(phenalenone\textsubscript{3}) based NIR OLED had an EQE of 0.007\% at \(\lambda_{\text{max}}\) = 1065 nm.\textsuperscript{70} The second class of NIR OLEDs is transition-metal complexes, similar to those used in the visible region. A recent report of an electrophosphorescent device that used a cyclometalated [(pyrenyl-quinolyl)\textsubscript{2}Ir(acac)] complex as the phosphor gave \(\lambda_{\text{max}}\) = 720 nm and an EQE of 0.1\%.\textsuperscript{76} More specifically, a subclass of phosphorescent metal-organic complexes, metalloporphyrins, has shown intense absorption and emission in the red-to-NIR region of the spectrum.\textsuperscript{77,78} There are a number of reports of OLEDs fabricated with PtOEP, PtTPP (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin, TPP = 5,10,15,20-tetra-phenylporphyrin), or analogues of these compounds as phosphorescent emitters, with emission maxima between 630 and 650 nm.\textsuperscript{35,79-86} Porphyrin chromophores with fused aromatic moieties at the \(\beta\)-pyrrole positions, for example, tetrabenzoporphyrrin (TBP), exhibit a bathochromic shift (relative to unsubstituted porphyrin) of the absorption and emission energy, owing to the expansion of the \(\pi\)-electronic system of the porphyrin core.\textsuperscript{87} The addition of bulky groups to the meso positions of the porphyrin macrocycles with \(\beta\)-substituted pyrroles leads to the formation of nonplanar porphyrins, and further red-shifts the absorption
Coordination of a heavy-metal atom increases the rate of the intersystem crossing between singlet and triplet states of the metalloporphyrins, thereby enhancing the rate of radiative decay from the triplet states. Considering all these reasons, π-extended Pt-porphyrin complexes such as Pt-tetraphenyltetrabenzoporphyrin (Pt-TPTBP) have been studied for NIR OLEDs with a reported maximum EQE of 8.5% at a peak wavelength of 770 nm. Analysis of the Pt-TPTBP complex by X-ray crystallography reveals a nonplanar molecular structure with a saddle-type distortion, similar to that found in other TPTBP derivatives. These Pt-porphyrins show relatively narrow phosphorescence emission bandwidths and high quantum yield in solution. But so far, to the best of our knowledge all of the NIR emitting Pt-porphyrins that have been incorporated into PLEDs or OLEDs have phosphorescence peaks below 900 nm.

In this chapter, based on the NIR emitting phosphorescent, Pt-TPTBP, we further extend the π-conjugation system by replacing the benzo- groups in the β-pyrrole positions with naphtha- and anthro- groups, which are Pt-tetraphenyl-tetranaphthoporphyrin (Pt-TPTNP) and Pt-tetraaryl-tetraanthroporphyrin (Pt-Ar₄TAP), to achieve emissions with even longer wavelengths into NIR region. The NIR OLEDs based on Pt-TPTNP have the emission wavelength peaked at ~900 nm and, when incorporated into OLEDs, a maximum EQE of 3.8% has been obtained, while the more conjugated Pt-Ar₄TAP based NIR OLEDs have further longer emission wavelength peaked at ~1000 nm and EQE up to 0.2%. This is the longest wavelength demonstrated to date for a triplet phosphor in an electroluminescent device.

The photophysics of various extended conjugation porphyrins have been previously investigated, and it has been demonstrated that substituents play a major
role in determining porphyrin photophysical properties.\textsuperscript{84,173-176} For example, Vinogradov, \textit{et al.} demonstrated that Pd-5,15-diphenyltetrabenzoporphyrin has a phosphorescence quantum yield of 0.15, whereas Pd-5,10,15,20-tetraphenyl-tetrabenzoporphyrin has a quantum yield of only 0.08.\textsuperscript{173} Furthermore, Beeby, \textit{et al.} have demonstrated an approximate doubling of solution $\phi_{em}$ from 0.11 to 0.21 for 5,10,15,20-tetrasubstituted free base porphyrins when monophenyl substituents are substituted for more bulky fluorene or terphenyl substituents.\textsuperscript{173,174} Drawing from these previous work, a family of Pt-tetrabenzoporphyrins (Pt-TBPs) incorporating 5,15-diaryl and 5,10,15,20-tetraaryl derivatives with varying substituent groups has been synthesized, and the diaryl derivatives display a 50% enhancement in solution quantum yield as compared to the tetraaryl derivatives.\textsuperscript{177} But when this family of Pt-TBPs is incorporated into NIR OLEDs, the device efficiencies show inconsistent trend of enhancement with that in solution, that the NIR OLEDs based on 5,15-diaryl derivatives show no enhancement of the device efficiencies compared to the 5,10,15,20-tetraaryl derivatives based devices. Then the devices based on this family of Pt-TBPs are further characterized through solid state electroluminescence transient lifetime measurements, and a strong correlation is observed between the EL lifetimes and device efficiencies. It was also found that the addition of 3,5-di-\textit{tert}-butylphenyl groups in place of phenyl groups on the benzoporphyrin ring periphery results in increased device efficiencies. A record high maximum EQE of 9.2\% is obtained for NIR OLEDs based on Pt-TBP with 5,10,15,20-tetraaryl groups, to which 3,5-di-\textit{tert}-butylphenyl groups attach (Pt-Ar$_4$TBP).

Finally, the aggregate effect of Pt-TBPs on EL efficiency is studied based on the two Pt-porphyrin molecules: Pt-Ar$_4$TBP, which has bulky end groups added in place of
the meso-aryl groups on the benzoporphyrin ring periphery, and the non-substituted counterpart, Pt-TPTBP. The extent of aggregation for the two molecules in devices is compared through the device efficiency decay rate with the increasing doping concentration of dopants.

This chapter is organized as follows. The experimental details on optical characterization, device fabrication and characterization are described in section 5-2. In section 5-3, we present the experimental results and discussion on the optical properties of the extended conjugation Platinum (II) porphyrins and performance of the NIR OLEDs. In section 5-4, we show the experimental results and discussion on the effect of molecular structure on EL efficiency in Platinum (II) tetrabenzoporphyrins (Pt-TBPs). Beginning with a brief introduction of triplet excited states decay and quenching models, we also study the solid state electroluminescence transient lifetime of the NIR OLEDs based on these Pt-TBP emitters in section 5-5. The aggregate effect of Pt-TBPs on EL efficiency is studied in section 5-6. Finally, we conclude in section 5-7.

5.2 Experimental Details

All the Pt(II) porphyrin molecules were synthesized and purified as reported\textsuperscript{177} by Jonathan Sommer in Dr. Kirk Schanze group in the Department of Chemistry at the University of Florida. He also measured the following solution photophysical data.

Absorption spectra were measured using a PerkinElmer Lambda 25 UV-vis spectrometer. The PL spectra of Pt-TBPs and Pt-TPTNP were obtained by excitation at the absorption maxima and recorded with an ISA SPEX Triax 180 spectrograph coupled to a Spectrum-1 liquid nitrogen-cooled charge coupled device (CCD) detector. This spectrometer has a relatively flat spectral response to 900 nm, although there is some loss in efficiency due to the grating, which is blazed in the visible region. For Pt-Ar\textsubscript{4}TAP,
a Spex Fluorolog II equipped with an InGaAs near-IR photomultiplier tube detector was used. The solution phosphorescence quantum yield was calculated relative to ZnTPP in CH$_2$Cl$_2$ ($\phi = 0.033$) according to a previously described method. The sample and actinometer solutions have matched optical density at the excitation wavelength, and the emission spectra were corrected for the spectrometer response prior to being used to compute the quantum yield. Solution lifetimes were determined from transient absorbance measurements. The transient absorption spectra were collected by using previously described laser systems for the visible and near-IR regions.

NIR OLED devices were fabricated on glass substrates commercially pre-coated with an indium tin oxide (ITO) anode (sheet resistance $\sim 20 \, \Omega/\square$). The cleaning procedure for substrates is already described in Chapter 4. All the layers (except those in the Pt-Ar$_4$TAP based device), including the cathode, were deposited by vacuum thermal evaporation at a base pressure of $1 \times 10^{-7}$ Torr following previously published procedures.\textsuperscript{39} To fabricate the OLED, a 40 nm thick hole transporting layer (HTL) of $\alpha$-NPD, an emissive layer (EML) consisting of host matrix doped with the NIR Pt-porphyrin emitters, an electron transport layer (ETL) of bathophenanthroline (BPhen), and a 1 nm thick LiF layer followed an Al cathode layer (50 nm thick) were successively deposited on the substrates. The emissive layer of all Pt-TBPs based OLEDs is Alq$_3$ with 4% Pt-TBPs and has the thickness of 25 nm, while the EML of Pt-TPTNP based OLEDs is 20 nm thick and consists of the CBP host doped with Pt-TPTNP. The thickness of the BPhen ETL was 80 nm for Pt-TBPs and varied from 100 nm to 120 nm for Pt-TPTNP based devices, respectively. More specifically, in one device of Pt-TPTNP, the entire BPhen ETL is nominally undoped (specified as the “undoped device”). In another device
(specified as the “n-doped device”), Cs was used to n-dope BPhen (BPhen:Cs = 1:0.2, molar ratio) except in the 15 nm layer adjacent to the EML. Cs has been shown to serve as an effective n-type dopant in BPhen to increase the conductivity of the ETL and improve the efficiency of electron injection from the cathode.\textsuperscript{178}

Pt-Ar\textsubscript{4}TAP could not be thermally evaporated due to its high molecular weight; therefore, Pt-Ar\textsubscript{4}TAP multi-layer OLEDs were constructed by spin casting a layer of Pt-Ar\textsubscript{4}TAP in PVK:PBD blend onto the PEDOT:PSS coated ITO/glass substrate, followed by thermal evaporation of a 40 nm thick electron transporting layer of BPhen or tris[3-(3-pyridyl)mesityl]borane (3TPYMB), a 1 nm thick LiF, and an Al cathode layer (100 nm thick). The film of PEDOT:PSS (Clevios P VP Al 4083) was deposited by spin-coating at 4000 RPM, and annealed on a hotplate in an argon glovebox for 20 minutes at 130°C (~40 nm thick). As the OLEDs were characterized in air without device encapsulation, a 200 nm thick MoO\textsubscript{x} overlayer is thermally evaporated to the surface of Pt-Ar\textsubscript{4}TAP devices, to improve the OLED device stability as they are exposed to the laboratory ambient for the short time period of testing and characterization. Individual solutions of poly(9-vinylcarbazole) (PVK, 20 mg/mL), 2-(4-tert-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD, 20 mg/mL), Pt-Ar\textsubscript{4}TAP (3.5 mg/mL) were prepared in anhydrous and deoxygenated chlorobenzene and stirred overnight. Solutions were combined to obtain PVK:PBD ratios varied from 6:4 to 7:3, and the doping concentration of Pt-Ar\textsubscript{4}TAP varied from 2% to 4%. The resulting solution mixtures were filtered with 0.45 μm PTFE (Whatman puradisc) filters and using a clean glass syringe they were directly deposited onto the PEDOT:PSS coated ITO/glass substrates. The solution concentrations were 12 or 9 mg/mL and then spin cast at 1000 or 2000 RPM for 60 s, both two parameters
changed for slightly different active layer thickness. The active layer thickness for 12 mg/mL solution spun coating at 1000 RPM was ~110 nm as determined by AFM. These solution processed film depositions and characterizations are done by Kenneth Graham in Dr. John Reynolds group in the Department of Chemistry at the University of Florida.

The deposition rates for the organic layers were 0.1-0.2 nm/s, as monitored by quartz crystal microbalances. The active device area was 4 mm² with the electrodes arranged in a cross-bar geometry, and each ITO/glass substrate featured four independently addressable device pixels. Alq₃ and BPhen were purchased from TCI America, 3TPYMB from Lumtec, α-NPD from e-Ray, and CBP from Springchem & Jadetextile Group Ltd. All organic materials were used as obtained except for α-NPD and BPhen, which were purified in house using vacuum gradient sublimation method for one to two cycles.¹⁴

Radiant emittance (R) – current density (J) – voltage (V) characteristics of the NIR OLEDs were measured in ambient using an Agilent 4155C semiconductor parameter analyzer and a calibrated silicon detector (Newport 818 UV). EL spectra of Pt-TBPs and Pt-TPTNP based devices were taken with the ISA SPEX Triax 180 spectrograph coupled to a Spectrum-1 liquid nitrogen cooled silicon CCD detector with the devices driven at a constant current using a Keithley 2400 source meter. For Pt-Ar₄TAP based OLEDs, a Spex Fluorolog II equipped with an InGaAs near-IR photomultiplier tube detector was used. But for the visible emission of this device, the CCD was still used. The radiant emittance was calibrated assuming Lambertian emission, and the EQE (ηₑₒₑ) and “wall plug” power efficiency (ηₚ) were derived based on the recommended methods.¹⁵ The organic layer thickness non-uniformity across the samples and run-to-
run variations typically lead to 5-10% error in device efficiencies. All measurements are averages over at least ten pixels and are presented along with standard deviations.

Electroluminescence transient lifetimes were measured by applying a 1 ms voltage pulse to the device. The voltages were created by a Tektronix AFG3101 function generator (100 MHz) and the magnitude of voltages was chosen to keep the current density at 10 mA/cm². The decay signals were captured by a Newport 818-UV photodetector which was connected with a Tektronix DPO3054 digital phosphor oscilloscope (500 MHz) for data acquisition. The electroluminescence decay was fitted to a bi-exponential decay function and the average lifetime was calculated by a standard method.¹⁷⁹-¹⁸¹

5.3 Extended Conjugation Platinum (II) Porphyrins

The molecular structures of the series of increasing π-conjugation phosphorescent Pt-porphyrins: Pt-TPTBP, Pt-TPTNP and Pt-Ar₄TAP, are shown in Figure 5-1.

![Molecular structures of increasing π-conjugation series of phosphorescent Pt-porphyrins: Pt-TPTBP, Pt-TPTNP and Pt-Ar₄TAP.](image)

Figure 5-1. Molecular structures of increasing π-conjugation series of phosphorescent Pt-porphyrins: Pt-TPTBP, Pt-TPTNP and Pt-Ar₄TAP.

The PL spectra of these Pt-porphyrins in toluene solutions are shown in Figure 5-2. As the π-system is extended across the series of Pt-TPTBP, Pt-TPTNP, and Pt-Ar₄TAP, the solution emission wavelength maxima shift from 773 to 891 to 1022 nm, respectively, as expected. Accompanying this wavelength shift is a decreasing
phosphorescence quantum yield ($\phi_{em}$) and decreasing lifetime ($\tau_{em}$) as predicted by the energy gap law.\textsuperscript{182-184} The PL quantum yield of Pt-TPTNP is measured to be 0.20, two times lower than Pt-TPTBP, whose PL quantum yield is 0.46. And Pt-Ar$_4$TAP shows even lower $\phi_{em}$ of 0.11. The solution PL lifetimes follow the trend as the PL quantum yield, in which the lifetime of Pt-TPTBP is 29.9 $\mu$s, and then decreases to 12.7 and 3.2 $\mu$s for Pt-TPTNP and Pt-Ar$_4$TAP, respectively. All these data including PL emission maxima, $\lambda_{max}^{em}$, PL quantum yields, $\phi_{em}$, and lifetimes, $\tau_{em}$ in the toluene solution are listed in Table 5-1 for comparison.

![Figure 5-2](image)

Figure 5-2. The photoluminescence spectra of Pt-TPTBP (solid lines), Pt-TPTNP (dashed lines) and Pt-Ar$_4$TAP (dash dotted lines) in toluene solutions.

The trend of decreased quantum yields and lifetimes is partially due to the increased non-radiative decay rate in these lower band gap molecules. To better prove this conclusion, the radiative and nonradiative decay rate constant, $k_r$ and $k_{nr}$ are calculated by the following equations:

$$\phi_{em} = k_r \times \tau_{em}$$  \hspace{1cm} (5-1)

$$k = 1/\tau_{em} = k_r + k_{nr}$$  \hspace{1cm} (5-2)
where $k$ is the total decay rate constant. The results of the calculated $k_r$ and $k_{nr}$ are also listed in Table 5-1. The non-radiative decay rate of Pt-Ar$_4$TAP is more than ten times higher than Pt-TPTBP, and four times higher than Pt-TPTNP, while the radiative decay rates of all three Pt-porphyrins are within the same order of magnitude.

Table 5-1. Photophysical data (PL emission maxima, $\lambda_{\text{max}}^\text{em}$, PL quantum yields, $\phi_{\text{em}}$, lifetimes, $\tau_{\text{em}}$, and radiative and non-radiative decay rate constant, $k_r$ and $k_{nr}$) for Pt-TPTBP, Pt-TPTNP and Pt-Ar$_4$TAP in deoxygenated toluene.

<table>
<thead>
<tr>
<th>Pt-porphyrins</th>
<th>$\lambda_{\text{max}}^\text{em}$ (nm)</th>
<th>$\phi_{\text{em}}$</th>
<th>$\tau_{\text{em}}$ (μs)</th>
<th>$k_r$ ($\times 10^{-2}$ μs$^{-1}$)</th>
<th>$k_{nr}$ ($\times 10^{-2}$ μs$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-TPTBP</td>
<td>773</td>
<td>0.46</td>
<td>29.9</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Pt-TPTNP</td>
<td>891</td>
<td>0.20</td>
<td>12.7</td>
<td>1.6</td>
<td>6.3</td>
</tr>
<tr>
<td>Pt-Ar$_4$TAP</td>
<td>1022</td>
<td>0.11</td>
<td>3.2</td>
<td>3.4</td>
<td>28</td>
</tr>
</tbody>
</table>

The solution $\phi_{\text{em}}$ value generally provides a good figure of merit to predict the efficiency of a series of structurally related chromophores in the OLEDs; therefore, a similar trend of decreasing OLED efficiencies across the series of Pt-TPTBP, Pt-TPTNP, and Pt-Ar$_4$TAP is expected as the emission is shifted into the near-IR region.

5.3.1 Near-IR OLEDs based on Pt-TPTNP

NIR OLEDs based on Pt-TPTBP was first fabricated to compare with the already reported results by Thompson and co-workers. The EL emission wavelength peaked at 773 nm and EQE can be achieved up to 8.0% in our devices. These results are very similar to what Thompson and co-workers have reported, considering the allowable deviation between different scientific labs probably due to the different film thickness calibrations of vacuum thermal evaporation method.$^{88,89}$

OLEDs based on the Pt-TPTNP were fabricated via vacuum thermal evaporation. The emissive layer (EML) consisting of CBP doped with Pt-TPTNP, was sandwiched between a hole transport layer (HTL) of $\alpha$-NPD and an electron transport layer (ETL) of
The \( R-J-V \) and EQE characteristics of Pt-TPTNP-based NIR OLEDs with various doping concentrations and ETL thickness are shown in Figure 5-3.

Figure 5-3. (color) A) Current density, \( J \), and the radiant emittance in the forward viewing directions, \( R \), as functions of the voltage, \( V \), for the devices based on Pt-TPTNP with various doping concentrations and ETL thickness. Cs was also used to \( n \)-dope the 100 nm ETL layer (\( n \)-doped device). B) External quantum efficiency, \( \eta_{\text{EQE}} \), of these devices as functions of \( J \). Inset: Power efficiency, \( \eta_P \), of the undoped and \( n \)-doped devices with 100 nm thick ETL and 8\% doping concentration, as functions of \( J \).

As mentioned in Chapter 4, the ETL thickness will affect the device efficiencies due to the microcavity effect in OLEDs. By using the 10\% doping concentration of Pt-TPTNP, the EQEs of devices achieve the maximum value as the ETL thickness is reduced from 120 nm to 100 nm, as shown in Figure 5-3B. Then, by using this optimal
ETL thickness of 100 nm, the doping concentration of Pt-TPTNP is varied to achieve a balance between the maximum energy transfer and minimum aggregate quenching. The doping concentration with maximum efficiency is found to be 8%, as shown in Figure 5-3B, by comparing the devices with doping concentration from 8% to 10%.

All these devices show close current densities and radiant emittance, as shown in Figure 5-3A. To increase the conductivity and improve the efficiency of electron injection from the cathode, Cs was also used to n-dope the 100 nm BPhen ETL layer (n-doped device). As shown in Figure 5-3A, at $V > 2.5$ V, the current density was approximately two orders of magnitude higher in the n-doped device, due to the significantly enhanced conductivity in the n-doped ETL compared with that in the nominally undoped 100 nm thick ETL. The undoped device shows a low turn-on voltage of approximately 2.2 V even though the BPhen ETL is rather thick (100 nm), which is further reduced to 2.0 V for the n-doped device. Maximum radiant emittances of 1.8 mW/cm$^2$ are obtained (at $V = 17$ V in the undoped device and $V = 12$ V in the n-doped device), which are similar to those obtained from our previously reported fluorescent NIR OLEDs in Chapter 4 that emit at shorter wavelengths (peak emissions from 700 nm to 815 nm).\textsuperscript{185,186}

For the undoped device with optimal doping concentration of 8% and ETL thickness of 100 nm, the EQE is relatively constant at low current densities and reaches a maximum of $\eta_{\text{EQE}} = (3.8 \pm 0.3)\%$ at $J \approx 0.1$ mA/cm$^2$; however, at $J > 1$ mA/cm$^2$, it decreases significantly with the increase of the current density to $\eta_{\text{EQE}} = 2.0\%$ at $J = 10$ mA/cm$^2$ and $\eta_{\text{EQE}} = 0.6\%$ at $J = 100$ mA/cm$^2$. The significant roll-off at higher current densities is likely due to the triplet-triplet exciton annihilation process that commonly occurs in phosphorescent OLEDs.\textsuperscript{187} The maximum power efficiency of the undoped
device is $\eta_P = (19 \pm 3) \text{ mW/W}$, achieved at low current densities ($J \approx 10^{-3} \text{ mA/cm}^2$), as shown in the inset of Figure 5-3B. Such efficiency is approximately three to ten times higher than the maximum $\eta_P$ of the NIR fluorescent OLEDs we mentioned earlier.\textsuperscript{185,186} These efficiencies are lower compared to Pt-TPTBP based devices, but are approximately proportional to the corresponding PL quantum yields of these two molecules (Table 5-1). Compared with the undoped device, the $n$-doped device has slightly lower quantum efficiencies with a maximum of $\eta_{EQE} = 3.3\%$. The maximum $\eta_P$ of the n-doped device is $\eta_P = 17 \text{ mW/W}$, also slightly lower than the undoped device; however the lower drive voltage resulted from the increased conductivity of the $n$-doped ETL leads to higher power efficiencies at $J > 10^{-2} \text{ mA/cm}^2$ for the $n$-doped device. For example, at $J = 1 \text{ mA/cm}^2$, $\eta_P = 12 \text{ mW/W}$ for the $n$-doped device, more than 40% higher than that of the undoped device ($\eta_P = 8.4 \text{ mW/W}$).

Figure 5-4. Normalized electroluminescence (EL) spectra, for NIR OLEDs based on Pt-TPTBP (solid line) and Pt-TPTNP (dashed line).

Figure 5-4 shows the EL spectra of the NIR OLEDs based on Pt-TPTNP as well as the Pt-TPTBP for comparison. The peak emission wavelengths for Pt-TPTBP and Pt-
TPTNP based devices are 773 nm and 891 nm, nearly identical to the corresponding PL peaks in solution (Table 5-1). It is noticed that the full width half maxima (FWHM) of the EL peaks of Pt-porphyrin based devices are in the range of 50-60 nm, much narrower than those of the fluorescent DAD oligomers based NIR OLEDs, which are usually in the range of 100-200 nm.

5.3.2 Near-IR OLEDs based on Pt-Ar₄TAP

The NIR OLEDs based on Pt-Ar₄TAP were fabricated with the device structure of ITO/PEDO:PSS/PVK:PBD:Pt-Ar₄TAP/BPhen or 3TPYMB/LiF/Al. Figure 5-5 schematically shows the energy level diagram of the NIR OLED based on Pt-Ar₄TAP, in which the electrode work functions and the HOMO/LUMO energies for PVK, PBD, BPhen and 3TPYMB are taken from the literature. PEDOT:PSS is served as the hole injection layer (HIL) while PBD and BPhen or 3TPYMB is served as the ETLs.

![Energy level diagram](image)

Figure 5-5. (color) Schematic energy level diagram of OLEDs based on Pt-Ar₄TAP. The energies (in eV) are measured from the vacuum level. The red and blue lines correspond to the HOMO/LUMO of PVK and PBD, respectively. The energy levels of Pt-Ar₄TAP are not indicated here.

The blend ratio of PVK and PBD, doping concentration of Pt-Ar₄TAP, and spin rate for the active layer, were studied to optimize the efficiency of devices. BPhen is used as
the ETL and the concentration of solution for active layer deposition is 12 mg/mL for all these devices. Figure 5-6A shows the J-V characteristics of these devices with different preparation recipes of the active layers. All the devices with active layers spun coated with 2000 RPM (Device 2, 3, 6, and 7) show lower turn-on voltages and higher injection currents than the corresponding devices with 1000 RPM spin rate (Device 1, 4, 5, and 8) which is as we predicted due to the reduced device thickness. Furthermore, by increasing the doping concentration of Pt-Ar₄TAP from 2% to 4% while keeping all the other parameters the same, the injection current densities of devices as well as the turn-on voltages are also decreased (for examples, Device 2 vs. 3, and Device 5 vs. 8), suggesting that the charge trapping by the dopant molecules cannot be neglected.

Finally, the blend ratios of PVK and PBD also play a role for the device performance that decreasing the portion of PBD in the blend active layer from 6:4 to 7:3 will enhance the current injection and then decrease the turn-on voltages.

Experiment has also been done to further decrease the PBD concentration in PVK:PBD blend to 8:2 in the devices, but no significant change has been observed. Overall, the highest current density and lowest turn-on voltage can be achieved by using spin rate of 2000 RPM, 2% doping concentration of Pt-Ar₄TAP and PVK:PBD ratio of 7:3 (Device 6), as shown in Figure 5-6A. The turn-on voltage of Device 6 is approximately 8 V, still much higher than the normal devices, mainly due to the thick active layer (~100 nm). So only 40 nm thick ETL layer is used here to avoid further increase of turn-on voltages. The EQE of these devices are also compared in Figure 5-6B. Device 6, which has the maximum current injection, also shows the highest EQE among all these devices, indicating the charge balance in Device 6 is also optimized.
Figure 5-6. (color) A) Current density, $J$, as functions of voltage, $V$, for Pt-Ar$_4$TAP based OLEDs with different preparation recipes of the active layer. B) External quantum efficiency, $\eta_{EQE}$ as functions of current density, $J$, for these OLEDs. The recipes for each device are listed in the table. The solution concentration is 12 mg/mL and ETL is BPhen for all the devices.

We also studied the effect of using different ETL layers by replacing BPhen with 3TPYMB, while maintaining the recipe of Device 6 which leads to the optimal current injection and device efficiency. As shown in Figure 5-5, 3TPYMB has a lower lying HOMO level than BPhen which can combine the holes within the active layer more effectively. 3TPYMB also has higher triplet energy than BPhen$^{43}$ which is beneficial to the exciton blocking. The $J$-$V$ characteristics of NIR OLEDs based on Pt-Ar$_4$TAP with different ETLs are shown in Figure 5-7A. The concentrations of the solution for

<table>
<thead>
<tr>
<th>Devices</th>
<th>PVK:PBD</th>
<th>Pt-Ar$_4$TAP%</th>
<th>Spin Rate (RPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6:4</td>
<td>2</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>6:4</td>
<td>2</td>
<td>2000</td>
</tr>
<tr>
<td>3</td>
<td>6:4</td>
<td>4</td>
<td>2000</td>
</tr>
<tr>
<td>4</td>
<td>6:4</td>
<td>4</td>
<td>1000</td>
</tr>
<tr>
<td>5</td>
<td>7:3</td>
<td>2</td>
<td>1000</td>
</tr>
<tr>
<td>6</td>
<td>7:3</td>
<td>2</td>
<td>2000</td>
</tr>
<tr>
<td>7</td>
<td>7:3</td>
<td>4</td>
<td>2000</td>
</tr>
<tr>
<td>8</td>
<td>7:3</td>
<td>4</td>
<td>1000</td>
</tr>
</tbody>
</table>
depositing active layers are also varied from 12 to 9 mg/mL to reducing the device thickness. As predicted, the devices spun coated with 9 mg/mL solution (Device 10 and 11) show higher current densities and lower turn-on voltages than the devices prepared with 12 mg/mL solution (Device 6 and 9).

![Figure 5-7](image)

<table>
<thead>
<tr>
<th>Devices</th>
<th>Solution c (mg/mL)</th>
<th>ETL</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>12</td>
<td>BPhen</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>3TPYMB</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>BPhen</td>
</tr>
<tr>
<td>11</td>
<td>9</td>
<td>3TPYMB</td>
</tr>
</tbody>
</table>

Figure 5-7. (color) A) Current density, \( J \), as functions of voltage, \( V \), for Pt-Ar\(_4\)TAP based OLEDs with different ETLs of BPhen or 3TPYMB and solution concentration. B) External quantum efficiency, \( \eta_{EQE} \) as functions of current density, \( J \), for these OLEDs. The recipes for each device are listed in the table. The PVK:PBD ratio is 7:3, the Pt-Ar4TAP is 2%, and spin rate is 2000 RPM for all these devices.

By comparing the effect of using different ETLs, it is found that the devices with BPhen as ETL have higher current density than 3TPYMB, while the turn-on voltages are almost the same. This can be attributed to the lower conductivity of 3TPYMB and higher injection barrier of electrons due to the lower lying LUMO energy level of 3TPYMB.\(^{43}\) As shown in Figure 5-7A, the turn-on voltage can be further reduced to 5.5-6.0 V by using 9
mg/mL solution for active layer deposition and either BPhen or 3TPYMB as the ETL. The EQE of these devices are shown in Figure 5-7B. It is found that the difference of solution concentration does not affect the device efficiencies appreciably. The devices with 3TPYMB as ETL show higher maximum EQE than the BPhen devices, but this is achieved at low current density of $J \approx 1$ mA/cm$^2$ and its roll-off at higher current densities is more significant than the BPhen devices. So at high current density ranges ($J > 10$ mA/cm$^2$), the devices with BPhen as ETL have higher EQE than the 3TPYMB devices as shown in Figure 5-7B. The power efficiencies can be predicted to have the same trend as the EQE comparison.

The device characterization of Device 10 with the optimal device structure (PVK:PBD ratio is 7:3, the doping concentration of Pt-Ar$_4$TAP is 2%, solution concentration is 9 mg/mL, spin rate for active layer is 2000 RPM, and BPhen as ETL) is summarized in Figure 5-8.$^{189}$ This device exhibits turn-on voltage of approximately 5.7 V. Maximum radiant emittance of 1.3 mW/cm$^2$ is achieved for this device at $V \approx 13$ V, as shown in Figure 5-8A. The EQE and power efficiency of this optimal device are shown in Figure 5-8B. This device has a maximum EQE of $\eta_{EQE} = (0.24 \pm 0.03)\%$ achieved at $J \approx 10$ mA/cm$^2$, slowly decreasing to $\eta_{EQE} = 0.14\%$ at $J = 500$ mA/cm$^2$. The maximum power efficiency is $\eta_P = (0.47 \pm 0.03)$ mW/W also achieved at $J \approx 10$ mA/cm$^2$. These efficiencies of EQE and power efficiency are lower than those expected from the quantum yield, which may originate from degradation or impurities.

It should be noted that the Pt-Ar$_4$TAP device does show some visible emission, as shown in Figure 5-8C, and it is thought that this could be due to degradation or impurities since the material is light sensitive and was also difficult to purify. The visible
Figure 5-8. A) Current density, $J$, and radiant emittance in the forward viewing directions, $R$, as functions of voltage, $V$, for the optimal NIR OLEDs based on Pt-Ar$_4$TAP. B) External quantum efficiency, $\eta_{EQE}$, and power efficiency, $\eta_P$, as functions of current density, $J$, for this device. C) Normalized electroluminescence (EL) spectra of this device.

emission is relatively broad with peak emission wavelength of ~440 nm, and the intensity is about 20% of that of the NIR peak at 1005 nm from Pt-Ar$_4$TAP. The peak emission wavelength is slightly blue-shifted compared to the corresponding PL peak in
solution. For the radiant emittance and EQE measurement and calculation, the visible emission from the Pt-Ar$_4$TAP device was not removed, which may result in the deviation to some extent. The measurement can be improved by using an 800 nm long-pass filter to remove the visible emission from the devices.

Through the extension of the $\pi$-system from Pt-TPTBP to Pt-TPTNP and Pt-Ar$_4$TAP, the electroluminescence was shifted up to 1005 nm, which is the longest wavelength demonstrated to date for a triplet phosphor in an electroluminescent device. These efficiencies of EQEs and power efficiency, and radiant emittance values achieved by NIR OLEDs based on this series of extended $\pi$-conjugation Pt-porphyrins are also some of the highest reported for OLEDs emitting in 750-1050 nm range.

5.4 Effect of Structure on EL Efficiency in Platinum (II) Tetrabenzoporphyrins

The photophysics of various expanded conjugation porphyrins have been previously investigated, and it has been demonstrated that substituents can play a major role in determining porphyrin photophysical properties.$^{84,173-176}$

Here, a family of Pt-tetrabenzoporphyrins (Pt-TBPs) incorporating 5,15-diaryl and 5,10,15,20-tetraaryl derivatives with varying substituent groups has been synthesized to provide insight into how structural variation of the expanded conjugation Pt-porphyrins impact their solution and solid state photophysics, and how these properties relate to the OLED performance.$^{189}$ The molecular structures of the series of Pt-porphyrins are shown in Figure 5-9.

The photophysical properties including solution PL quantum yields, $\phi_{em}$, and lifetimes, $\tau_{em}$, of these Pt-TBPs are listed in Table 5-2. Radiative and nonradiative decay rate constant, $k_r$ and $k_{nr}$ are also calculated by equation 5-1 and 5-2 shown above.
Figure 5-9. Molecular structures of Pt-porphyrins: Pt-TPTBP, Pt-Ar$_4$TBP, Pt-DPTBP and Pt-Ar$_2$TBP, Pt-TAr$_2$TBP, and Pt-Ar$_2$OPrTBP.

As shown in Table 5-2, the solution $\phi_{em}$ and $\tau_{em}$ values are 50-60% larger for the di-substituted 5,15-diaryl porphyrin derivatives relative (except Pt-DPTBP) to the 5,10,15,20-tetraaryl substituted porphyrins. The tetra-substituted Pt-porphyrins have a non-planar molecular structure with a large degree of out of plane (saddle-type) distortion, while the less substituted diaryl porphyrins still keep the planar structure in spite of in-plane distortion due to the insertion of meso-aryl groups perpendicular to the molecular plane.$^{173,176,190-192}$ The nonplanar deformation will dramatically enhance the nonradiative decay of triplet states of Pt-porphyrins, similar to the Pd porphyrins reported earlier.$^{173}$ This is consistent with the calculated results of $k_r$ and $k_{nr}$ values listed in Table 5-2. The nonradiative decay rates of di-substituted Pt-porphyrins are approximately 2-3 times lower than the tetra-substituted Pt-porphyrins, while the radiative decay rates are within 20% difference for all the Pt-porphyrins.
Furthermore, meso-aryl-substituted Pt-porphyrins have been reported to be rather poor red-light-emitting dyes in OLEDs, which is mainly ascribed to some conjugative effect of the meso-aryl substituents that stems from their somewhat free rotational movement. It is believed that such a conjugative interaction of meso-aryl substituents will also accelerate the nonradiative decay of the triplet excited state of the Pt-porphyrins.\textsuperscript{193,194} The di-substituted Pt-porphyrins now can decrease one pair of meso-aryl substituents and also their free rotational movement, by which the nonradiative decay rate will also be reduced. So both the lack of out-of-plane distortion and less rotation of the meso-aryl groups for di-substituted Pt-porphyrins can suppress the nonradiative decay rate while the radiative rate does not change, leading to the much higher solution quantum yields and lifetimes of di-substituted Pt-porphyrins compared to the tetra-substituted ones.

Table 5-2. Photophysical data (PL quantum yields, \(\phi_{\text{em}}\), lifetimes, \(\tau_{\text{em}}\), radiative and nonradiative decay rate constant, \(k_r\) and \(k_{nr}\)) measured in toluene and device characteristics (maximum EQEs, \(\eta_{\text{EQE, max}}\), and EL lifetimes, \(\tau_{\text{EL}}\)) for Pt-TPTBP, Pt-Ar\(_4\)TBP, Pt-DPTBP, Pt-Ar\(_2\)TAP, Pt-TAr\(_2\)TBP, and Pt-Ar\(_2\)OPrTBP. The EL lifetimes are measured at 10 mA/cm\(^2\).

<table>
<thead>
<tr>
<th>Pt-porphyrins</th>
<th>(\phi_{\text{em}})</th>
<th>(\tau_{\text{em}}) ((\mu)s)</th>
<th>(k_r) ((\times 10^{-2}) (\mu)s(^{-1}))</th>
<th>(k_{nr}) ((\times 10^{-2}) (\mu)s(^{-1}))</th>
<th>EL (\tau_{\text{EL}}) ((\mu)s)</th>
<th>(\eta_{\text{EQE, max}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-TPTBP</td>
<td>0.44</td>
<td>29.9</td>
<td>1.5</td>
<td>1.8</td>
<td>-</td>
<td>8.0 ± 0.5</td>
</tr>
<tr>
<td>Pt-Ar(_4)TBP</td>
<td>0.44</td>
<td>32.0</td>
<td>1.4</td>
<td>1.7</td>
<td>27.0</td>
<td>9.2 ± 0.7</td>
</tr>
<tr>
<td>Pt-DPTBP</td>
<td>0.40</td>
<td>28.0</td>
<td>1.4</td>
<td>2.2</td>
<td>24.0</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>Pt-Ar(_2)TBP</td>
<td>0.65</td>
<td>53.0</td>
<td>1.2</td>
<td>0.7</td>
<td>26.5</td>
<td>7.8 ± 0.5</td>
</tr>
<tr>
<td>Pt-TAr(_2)TBP</td>
<td>0.58</td>
<td>51.7</td>
<td>1.1</td>
<td>0.8</td>
<td>19.2</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>Pt-Ar(_2)OPrTBP</td>
<td>0.60</td>
<td>51.8</td>
<td>1.2</td>
<td>0.7</td>
<td>23.6</td>
<td>7.0 ± 0.5</td>
</tr>
</tbody>
</table>

To further reduce the effect of rotational freedom of meso-aryl substituents, steric bulky end groups are added in place of these meso-aryl groups on the benzoporphyrin ring periphery, to severely restrict the rotational freedom of meso-aryl substituents. These steric bulky end groups can also prevent the \(\pi-\pi\) stacking interactions and then aggregation when in the solid state films. This is beneficial for application in devices.
because the decreased aggregation of molecules will reduce the triplet-triplet annihilation processes in the solid state. We first add 3,5-di-tert-butylphenyl groups to each of meso-aryl substituents in the Pt-TBPs for both di- and tetra-substituted Pt-TBPs. With these bulky end groups, Pt-Ar₄TBP and Pt-Ar₂TBP both have higher quantum yields and lifetimes in the solution compared to their non-bulky substituted counterpart. Especially for Pt-Ar₂TBP, the lifetime in the solution is almost doubled of that of Pt-DPTBP. Molecules with even bulkier end groups providing even significant restriction effect are also synthesized based on the di-substituted Pt-TBPs, which are Pt-TAr₂TBP and Pt-Ar₂OPrTBP. But the solution quantum yields and lifetimes are not obviously increased compared to Pt-Ar₂TBP, which may indicate the 3,5-di-tert-butylphenyl groups already have enough size to effectively restrict the rotation of meso-aryl substituents.

Based on the solution behavior of the above Pt-TBPs, we predict that the di-substituted Pt-TBPs with bulky end groups to the meso-aryl substituents would give rise to more efficient NIR OLEDs compared to the existing OLEDs based on Pt-TPTBP. Figure 5-10A shows the EL spectra of the NIR OLEDs based on Pt-TPTBP, Pt-Ar₄TBP, Pt-DPTBP and Pt-Ar₂TBP. The structural modifications of these Pt-TBPs do not shift the emission peaks of the corresponding devices, all at wavelengths of 773-777 nm. The two di-substituted Pt-TBPs based devices have very narrow emission peaks with FWHM of only 40 nm, 50% narrower than the tetra-substituted Pt-TBPs based devices. This may be attributed to the out-of-plane distortion of tetra-substituted Pt-TBPs. The host emission of Alq₃ is completely quenched for all the four devices and only emission from the dopant molecules is observed, as shown in Figure 5-10A.
Figure 5-10. (color) A) Normalized electroluminescence (EL) spectra of the NIR OLEDs based on Pt-TPTBP (solid red squares), Pt-Ar$_4$TBP (solid blue triangles), Pt-DPTBP (open black circles) and Pt-Ar$_2$TBP (open green diamonds). B) Current density, $J$, and radiant emittance in the forward viewing directions, $R$, as functions of voltage, $V$, for these devices.

The $J$-$V$ characteristics of these OLEDs are shown in Figure 5-10B. All the four devices exhibit very close turn-on voltage of approximately 2.3 V. The tetra-substituted Pt-TBPs based OLEDs show higher current densities than the di-substituted Pt-TBPs devices, while the two devices within the same category do not show too much difference of the current injection. Accordingly, the tetra-substituted Pt-TBPs based OLEDs also exhibit higher radiant emittances than the di-substituted Pt-TBPs devices, especially at voltages from 3-7 V. The maximum radiant emittances of 3.4 and 4.4
mW/cm$^2$ are achieved for the Pt-TPTBP and Pt-Ar$_4$TBP based devices, respectively, while the Pt-DPTBP and Pt-Ar$_2$TBP based devices show the values of 2.1 and 3.0 mW/cm$^2$, all at $V = 15$ V.

Figure 5-11 shows the dependencies of $\eta_{EQE}$ and $\eta_P$ on the current density for NIR OLEDs based on these four Pt-TBPs. NIR OLEDs based on Pt-Ar$_4$TBP exhibit the highest EQE and power efficiencies while the efficiencies for Pt-TPTBP based devices are slightly lower. This result is consistent with the solution photophysical data of these two Pt-porphyrins. Pt-DPTBP based devices have the lowest efficiencies which are also in agreement with its lowest solution quantum yield and lifetime.

Figure 5-11. (color) External quantum efficiency, $\eta_{EQE}$, and power efficiency, $\eta_P$, of the NIR OLEDs based on Pt-TPTBP (solid red squares), Pt-Ar$_4$TBP (solid blue triangles), Pt-DPTBP (open black circles) and Pt-Ar$_2$TBP (open green diamonds) as functions of $J$.

To our surprise, not like the solution photophysical data has shown for Pt-Ar$_2$TBP that the solution quantum yield and lifetime are much higher than the other three Pt-
TBPs, the OLEDs based on Pt-Ar₂TBP have maximum EQE efficiency approximately 15% lower than Pt-Ar₄TBP based devices, and only close to the Pt-TPTBP based devices. It indicates that the trends observed when comparing the τ_em and ϕ_em values for the series of Pt-TBPs in solution do not carry over to the corresponding efficiencies of devices, in which these Pt-TBP molecules are in solid state films mixed with host matrix. Thus, while the solution photophysical data gives rise to the prediction that the di-substituted porphyrins will give more efficient electroluminescence in the devices, the device results contradict this, suggesting that the photophysical behaviors are different while in the solution and in the solid state. A maximum EQE of $\eta_{EQE} = (9.2 \pm 0.7)\%$ is achieved at $J \approx 10^{-2}$ mA/cm², slowly decreasing to $\eta_{EQE} = 4.0\%$ for $J$ up to 10 mA/cm², which is still over 40% of the maximum value. The OLEDs based on Pt-TPTBP and Pt-Ar₂TBP have slightly lower EQEs of $\eta_{EQE} = (8.0 \pm 0.5)\%$ and $(7.8 \pm 0.5)\%$, respectively, while Pt-DPTBP based devices show significantly lower efficiencies than the other three OLEDs, achieved of $\eta_{EQE} = (5.0 \pm 0.3)\%$.

The bulkier di-substituted Pt-porphyrins, Pt-TAr₂TBP and Pt-Ar₂OPrTBP, were also used for NIR OLEDs and compared with the Pt-Ar₂TBP derivative, as shown in Figure 5-12. These two molecules have similar solution photophysical behavior with Pt-Ar₂TBP as shown in Table 5-2. However, the bulkier substituents to the benzoporphyrin ring periphery may lead to further suppression of triplet-triplet annihilation due to decreased porphyrin/porphyrin interactions. The EL spectrum of Pt-TAr₂TBP based devices shows the same emission peak of 777 nm with the Pt-Ar₂TBP based devices but the emission is broader, as shown in Figure 5-12A. The emission peak wavelength red shifts to 792 nm for the NIR OLEDs based on Pt-Ar₂OPrTBP. As shown in Figure 5-12B, these two
Figure 5.12. (color) A) Normalized electroluminescence (EL) spectra of the NIR OLEDs based on Pt-TAr₂TBP (red) and Pt-Ar₂OPrTBP (blue). The EL spectrum of NIR OLEDs based on Pt-Ar₂TBP (black) is also shown for comparison. B) Current density, \( J \), and radiant emittance in the forward viewing directions, \( R \), as functions of voltage, \( V \), for these two devices. C) External quantum efficiency, \( \eta_{EQE} \), and power efficiency, \( \eta_{P} \), as functions of current density, \( J \), for these two devices.
devices both have close turn-on voltage of approximately 2.3 V to that of Pt-Ar$_2$TBP based devices and the maximum radiant emittances of 1.9 and 3.2 are achieved at $V = 15$ V for Pt-TAr$_2$TBP and Pt-Ar$_2$OPrTBP based devices, respectively, both lower than the Pt-Ar$_2$TBP based devices. Figure 5-12C shows the EQE and power efficiencies of these two devices. The Pt-Ar$_2$OPrTBP based device has a maximum EQE of $\eta_{EQE} = (7.0 \pm 0.4)\%$ achieved at $J \approx 10^{-2}$ mA/cm$^2$, while the EQE for Pt-TAr$_2$TBP based device is much lower, with a maximum of $\eta_{EQE} = (3.2 \pm 0.3)\%$ at $J \approx 10^{-2}$ mA/cm$^2$, although its roll-off at higher current densities is less significant.

The maximum power efficiency is $\eta_P = (37 \pm 3) \text{ mW/W}$ for the Pt-Ar$_2$OPrTBP based device, and is $(16 \pm 2) \text{ mW/W}$ for the Pt-TAr$_2$TBP based device, both achieved at low current densities ($10^{-3} < J < 10^{-2}$ mA/cm$^2$). Not like the similar solution behaviors for these two molecules with Pt-Ar$_2$TBP, these efficiencies for the devices based on these two molecules are all lower than the Pt-Ar$_2$TBP based devices especially for the Pt-TAr$_2$TBP devices, which only has less than 50% of the maximum EQE of Pt-Ar$_2$TBP based devices. This is not the first time the disagreement between solution photophysical data and device efficiencies has been found, as we have previously found that Pt-Ar$_2$TBP based devices exhibit a lower EQE than the solution photophysical data would indicate.

5.5 Electroluminescence Transient Lifetime of Devices

The disagreement between solution photophysical data and device efficiencies has been found previously. The trends observed when comparing the $\tau_{em}$ and $\phi_{em}$ values for the series of Pt-TBPs in solution do not carry over to the corresponding efficiencies of devices based on these molecules, in which these Pt-TBP molecules are in solid state
films mixed with host matrix. To explain these results and better evaluate the device performance in the future, the photophysical data such as quantum yield and lifetime measured in solid state instead of in solution should be used, so that they have the most similar situation as that in devices. Therefore in this section, we did the transient analysis of organic electrophosphorescence for the NIR OLEDs based on the series of Pt-TBPs shown in Figure 5-9.189

5.5.1 Theory

First, we consider the simplest situation that the triplet excited states in phosphor, $[^3T^*]$, decay naturally through radiative and non-radiative ways, without any possible quenching paths. The concentration of triplet excitons is determined by the following equation:

$$\frac{d[^3T^*]}{dt} = -k_T[^3T^*]$$

where $k_T$ is the total triplet exciton decay rate constant and has the following relation with phosphorescent recombination lifetime, $\tau$:

$$\tau = \frac{1}{k_T} = \frac{1}{k_r + k_{nr}}$$

Assuming that the power intensity ($I$) is linearly proportional to the concentration of excited states, then the phosphorescent emission intensity can be determined by solving the Equation 5-3:

$$I(t) = I_0 \exp(-t/\tau)$$

It is a mono-exponential decay for the situation that the triplet excited states only naturally decay, without any other ways to quench the triplet excitons.
Usually, one pronounced characteristics of electrophosphorescence is a roll-off efficiency at high current densities. It has been noted that the onset of this roll-off occurs at increasing current densities as the transient phosphorescent lifetime is decreased. Hence the phosphor Ir(ppy)$_3$ with a $\sim$500 ns excited-state lifetime, has a significantly higher quantum efficiency at typical operating current densities of $J \approx 1$ mA/cm$^2$ than does PtOEP, with a lifetime of $\sim$30 µs.

A possible explanation is that long transient lifetimes increase the likelihood for saturation of phosphorescent sites. Thus, devices incorporating a conductive organic host materials doped with Ir(ppy)$_3$ saturate at higher current densities than similar PtOEP-doped devices. However, the onset of the efficiency roll-off ($\sim 1$ mA/cm$^2$ for PtOEP and $\sim 100$ A/cm$^2$ for Ir(ppy)$_3$) occurs at much lower current density than is required to fully saturate phosphorescent sites with a density of $\sim 10^{19}$ cm$^{-3}$. We would also expect that saturation of phosphorescent sites would lead to an efficiency roll-off proportional to $1/J$, where $J$ is the current density. But at the current densities of interest, the roll-off is much more gradual. Thus, saturation alone cannot explain the observed behavior. Rather, the observations are consistent with triplet-triplet ($T-T$) annihilation dominating electrophosphorescence until relatively high current densities. For simplicity of analysis we assume that only guest triplets participate in $T-T$ annihilation, which will be another pathway of triplet loss. So Equation 5-3 then can be re-written as:

$$\frac{d[^3T^*]}{dt} = -k_T[^3T^*] - \frac{1}{2} k_{TT}[^3T^*]^2$$

(5-6)

where $k_{TT}$ is triplet-triplet annihilation rate constant. By solving the Equation 5-6, the phosphorescent emission intensity can be written as:
\[ I(t) = \frac{I_0}{(1 + K\tau)e^{t/\tau} - K\tau}, \quad K = \frac{1}{2}k_{TT}[^3T^*(0)] \]  

(5-7)

where \([^3T^*(0)]\) is the initial concentration of triplet excitons. Since only the triplet-triplet annihilation of guest triplets is considered in Equation 5-6, it means, the host triplet states should be much higher than that of guest, so that the triplets can be well confined on guest. But if there is only small energy difference between the host and guest triplet states, \(T-T\) annihilation will be present in both the host and guest, and that energy transfer between the two species is responsible for the multiple lifetimes needed to model the transient decays.\(^{187}\)

An alternative model for quenching is triplet-polaron annihilation.\(^{114,195}\) The concentration of triplet excitons can be determined by the following equation:\(^{114,195}\)

\[ \frac{d[^3T^*]}{dt} = -k_T[^3T^*] - k_{TP}[^3T^*][h] \]  

(5-8)

where \(k_{TP}\) is triplet-polaron annihilation rate constant, \([h]\) is the density of trapped holes. By solving the Equation 5-8, the phosphorescent emission intensity can be written as:

\[ I(t) = I_0[(1 - [h]/N)\exp(-k_T t) + [h]/N\exp(-(k_T + k_{TP}[h])t)] \]  

(5-9)

where \(N\) is the total number of guest molecules. Equation 5-9 can be re-written as:

\[ I(t) = I_1\exp(-t/\tau_1) + I_2\exp(-t/\tau_2) \]  

(5-10)

where: \(\tau_1 = \frac{1}{k_T}, \tau_2 = \frac{1}{k_T + k_{TP}[h]} \)  

(5-11)

It is a bi-exponential decay that one component of the transient lifetimes is the natural decay lifetime, \(\tau_1\), and the other component \(\tau_2\), obviously smaller than \(\tau_1\), originating
from the quenching of triplet excitons by guest molecule cations. The average transient lifetime, $\tau_{\text{avg}}$, can be calculated as follows:\textsuperscript{179-181}

$$\tau_{\text{avg}} = \sum_i A_i \tau_i = A_1 \tau_1 + A_2 \tau_2, \quad A_i = I_i / \sum_i I_i$$  \hspace{1cm} (5-12)

5.5.2 Transient Analysis of NIR OLEDs based on Pt-TBPs

Here, electroluminescence transient lifetimes of near-IR OLEDs based on the series of Pt-TBPs shown in Figure 5-9 were measured by applying a very short (1 ms) voltage pulse to the devices based on these Pt-TBPs and the phosphorescence decay signals of triplet excited states then can be captured to extract the EL lifetimes of the Pt-TBPs in devices. In this measurement, the Pt-TBP molecules are in the solid state films mixed with host matrix, and excitons are formed by binding of electrically injected holes and electrons. Therefore, it may provide the best estimation for the behaviors happened in devices.

Figure 5-13 shows the phosphorescence decay of Pt-Ar$_4$TBP, Pt-DPTBP and Pt-Ar$_2$TBP in their corresponding NIR OLEDs. The devices have exactly the same structures as mentioned above, and are operated in ambient at the constant current density of 10 mA/cm$^2$. The decay curves are fitted to a bi-exponential function as recommended by literature\textsuperscript{89} and the average EL transient lifetimes can be calculated by Equation 5-12. The fitting results are also shown in the inset of Figure 5-13. The bi-exponential function has a very good fitting agreement with the measured curves. The EL lifetimes of Pt-Ar$_4$TBP, Pt-Ar$_2$TBP and Pt-DPTBP are measured to be 27.0, 26.5 and 24.0 $\mu$s, respectively. Note that the EL lifetime of Pt-Ar$_2$TBP in devices decreases by 50% of the value in the solution while the EL lifetimes for the other two molecules are only slightly decreased. Pt-Ar$_2$TBP does not display a longer EL lifetime than Pt-Ar$_4$TBP
as was observed in the solution PL lifetimes, which is in good correlation with the trend for OLEDs efficiencies that Pt-Ar\textsubscript{2}TBP based devices did not show higher efficiencies than the Pt-Ar\textsubscript{4}TBP devices.

![Decay curves for different complexes](image)

Figure 5-13. (color) Phosphorescence decay of Pt-Ar\textsubscript{4}TBP, Pt-DPTBP and Pt-Ar\textsubscript{2}TBP in their corresponding NIR OLEDs operated at current density of 10 mA/cm\textsuperscript{2}. The experimental measured curves are shown in red lines and the fitting curves are shown in blue lines. The fitting results are also shown in the inset. The unit for $\tau_1$, $\tau_2$ and $\tau_{avg}$ are $\mu$s, and $A_1$ and $A_2$ are unitless.
The disagreement between solution photophysical data and device efficiencies for Pt-TAr$_2$TBP and Pt-Ar$_2$OPrTBP can also be explained by the EL lifetime measurement results. As shown in Figure 5-14, Pt-TAr$_2$TBP exhibit a much lower EL lifetime of 19.2 μs compared to the Pt-Ar$_2$TBP, consistent with the much lower device efficiencies for Pt-TAr$_2$TBP based OLEDs. The reason for the significant decrease in EQE from Pt-Ar$_2$TBP to Pt-TAr$_2$TBP is not known; it is possible that these compounds were decomposed to some extent in the thermal vapor deposition process (e.g., perhaps by loss of one or more of the aryl substituent groups). Pt-Ar$_2$OPrTBP has the EL lifetime of
23.6 μs, also lower than Pt-Ar₂TBP. The comparison of the EL lifetimes well matches the difference between the OLEDs based on these two molecules. The EL lifetimes measured at current density of 10 mA/cm² and maximum EQE for the NIR OLEDs based on the series of Pt-TBPs are summarized in Table 5-2.

5.6 Aggregation Effect of Pt-TBPs on EL Efficiency

Previously in Chapter 4, we have studied the NIR OLEDs with different doping concentration based on donor-acceptor-donor oligomers. The doping concentrations of those emitters need to be appropriately adjusted to achieve the balance between the maximum energy transfer and minimum aggregate quenching. One way to reduce the aggregation of dopants is to change the stacking and interaction of dopant molecules. For some molecules in the series of Pt-TBPs, for example, Pt-Ar₄TBP, bulky end groups are added in place of the meso-aryl groups on the benzoporphyrin ring periphery, compared to the non-substituted Pt-TPTBP. These bulky end groups can prevent the π-π stacking interactions of molecules and therefore molecular aggregation when in the solid state films and devices.

The aggregate effect of Pt-TPTBP and Pt-Ar₄TBP based NIR OLEDs is studied by varying the doping concentration of these two Pt-TBPs in devices from 2% to 12%. Except for the doping concentration of NIR emitters, the device structure for both molecules is exactly the same as that used in previous sections of this chapter. The maximum EQE for the devices with different doping concentrations are shown in Figure 5-15. The curves for both Pt-TPTBP and Pt-Ar₄TBP based devices exhibit the same trend that the EQE of devices decrease with the increasing doping concentration of doped Pt-TBPs, which is obviously due to the aggregate quenching as we discussed.
Figure 5-15. External quantum efficiency, $\eta_{\text{EQE}}$ of OLEDs based on two Pt-TBPs: Pt-TPTBP (black squares) and Pt-Ar$_4$TBP (red triangles) as a function of doping concentration, $x$ ($x = 2\%, 4\%, 8\% \text{ and } 12\%$), of these NIR emitters.

But the decay rates, which can be represented by the slopes of the efficiency curves, are different between the Pt-TPTBP and Pt-Ar$_4$TBP based OLEDs, indicating the different extent of aggregation effect between these two molecules in devices. For example, as the doping concentration is increased from 2% to 12%, the EQEs of Pt-Ar$_4$TBP based devices drops from 9.3% to 7.9%, approximately 15% decrease, but Pt-TPTBP based devices show 35% decrease of EQEs from 8.2% to 5.3%, more than two times higher than that of Pt-Ar$_4$TBP based devices. Especially, when the doping concentration is increased from 8% to 12%, the EQE for Pt-Ar$_4$TBP based devices almost stay the same with less than 5% efficiency dropoff, while Pt-TPTBP based devices still show significant decrease of EQE by approximately 20%. This means, by adding the bulky end groups in place of the meso-aryl groups on the benzoporphyrin ring periphery, the bulkier Pt-Ar$_4$TBP exhibits much less significant aggregate than Pt-TPTBP in the devices.
5.7 Summary

In this chapter, we have demonstrated the incorporation of a family of π-extended Pt-porphyrins, including the novel Pt-Ar$_4$TAP derivative, into NIR OLEDs. Through the extension of the π-system to Pt-Ar$_4$TAP the electroluminescence was shifted to 1005 nm, which is the longest wavelength demonstrated to date for a triplet phosphor in an electroluminescent device. The photophysical and OLED data on this series of π-extended Pt-porphyrins were compared, revealing decreasing solution $\phi_{em}$ and device efficiency as the π-system is extended and the emission is bathochromically shifted from 770 nm to 1005 nm.

The photophysics of a series of variously substituted Pt-tetrabenzoporphyrins were characterized both in solution and solid state and compared with their performance in OLEDs. Although relatively large differences in $\phi_{em}$ and $\tau_{em}$ between di- and tetra-substituted Pt-TBPs were observed in solution, the difference in $\tau_{em}$ was barely found in host matrix of devices. The results of this study clearly demonstrate that the large differences observed for the solution $\phi_{em}$ do not directly correlate with the performance of the chromophores in devices. It was also found that the addition of 3,5-di-tert-butylphenyl groups in place of phenyl groups on the benzoporphyrin ring periphery results in increased device efficiency; however, further increasing the size of the substituents to bulkier groups (such as terphenyl) does not improve the device performance. Although the efficiency improvements obtained with the di-substituted Pt-benzoporphyrins were not as high as predicted by their solution $\phi_{em}$ values, the NIR OLEDs based on the series of di-substituted Pt-TBPs still achieve very high efficiencies with maximum EQE up to 7-8% in the near-IR emission range. A record high EQEs
were finally obtained by OLEDs based on Pt-Ar₄TBP emitting at the peak wavelength of 773 nm with EQE of 9.2%.

Finally, the aggregate effect of Pt-TBPs on EL efficiency is studied based on the two Pt-porphyrin molecules: Pt-Ar₄TBP, which has bulky end groups added in place of the meso-aryl groups on the benzoporphyrin ring periphery, and the non-substituted counterpart, Pt-TPTBP. By comparing the efficiency decay rate with the increasing doping concentration of the two emitters, we find that the bulkier Pt-Ar₄TBP exhibits much less significant aggregate than Pt-TPTBP in the devices.
CHAPTER 6
ULTRA-VIOLET ORGANIC LIGHT-EMITTING DEVICES

6.1 Introduction to UV OLEDs

While research efforts remain strong to develop organic materials that emit visible light, we have shown the promising results of efficient OLEDs with near-IR emission based on fluorescent donor-acceptor-donor oligomers and phosphorescent Pt-porphyrins, with record high EQE up to 9.2% and emission peak wavelength over 1 μm. Another interest has recently turned to organic systems that emit at the other end of the visible range, the shorter wavelengths - from the deep blue, through the violet, to the ultraviolet regions. Ultraviolet (UV) to deep blue organic light-emitting diodes (OLEDs) have found, or are sought for, applications in biological and chemical sensing,\textsuperscript{90,91} sterilization, high-density information storage devices,\textsuperscript{92} and full-color light-emitting displays.\textsuperscript{93,94} Recently, there have been several reports\textsuperscript{95-104} of high efficiency fluorescent blue-to-violet OLEDs with a peak emission wavelength in the range of 400-480 nm that possess maximum EQE values up to 3-6%, although the shorter wavelength emission generally leads to lower device efficiencies. Despite a number of examples of deep blue to UV emitting OLEDs based on organic fluorescent emitters, including small molecules\textsuperscript{101-108} and polymers,\textsuperscript{99,100,109,110} only a few\textsuperscript{106,108} realize the device emission peak wavelengths below 400 nm, which can be considered as the UV emission, with external quantum efficiencies (EQE) greater than 1%. However, these so-called UV OLEDs still have relatively broad emission peaks, with emission tail extending as far as to the longer wavelength ranges of 450-550 nm. Table 6-1 lists some of the existing blue-violet-UV OLEDs in the literature. The challenges of fabricating UV OLEDs lie in two parts: one is the molecular design of organic materials
capable of efficient UV emission,\textsuperscript{106} and the other is appropriately designed device structure,\textsuperscript{108,111,112} where both hole and electron carriers are injected into a wide energy band gap UV emitting material and non-UV emissions from longer wavelength emitting materials need to be prevented. So here in this dissertation, highly sought are organic materials that can exploit the donor-acceptor concept\textsuperscript{105,107} to achieve emissive color tunability and provide high efficiency and brightness in the UV to violet region, and device structures with appropriate energy levels alignment.

Table 6-1. List of some existing blue (B), blue-violet (B-V) and ultraviolet (UV) OLEDs based on different emitters including small molecules and polymers.

<table>
<thead>
<tr>
<th>Emitters</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Claimed Emission</th>
<th>QY</th>
<th>Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO-PPP</td>
<td>425</td>
<td>B</td>
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<td>2.0%</td>
<td>99</td>
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<tr>
<td>PPP</td>
<td>424</td>
<td>B-V</td>
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<td>100</td>
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<tr>
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<td>B-V</td>
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<td>$p$-BPD</td>
<td>415</td>
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<td>1.2%</td>
<td>102</td>
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<tr>
<td>$p$-TTA</td>
<td>435</td>
<td>B-V</td>
<td>-</td>
<td>2.8%</td>
<td>103</td>
</tr>
<tr>
<td>F$_2$PA</td>
<td>405</td>
<td>B-V</td>
<td>0.56</td>
<td>2.0%</td>
<td>103</td>
</tr>
<tr>
<td>PFFA</td>
<td>422</td>
<td>B</td>
<td>0.76</td>
<td>1.1%</td>
<td>106</td>
</tr>
<tr>
<td>Bifluorene</td>
<td>374,392</td>
<td>UV</td>
<td>0.70</td>
<td>3.6%</td>
<td>106</td>
</tr>
<tr>
<td>2SBFN</td>
<td>381</td>
<td>UV (film)</td>
<td>0.70</td>
<td>2.0%</td>
<td>108</td>
</tr>
<tr>
<td>indoles</td>
<td>443</td>
<td>B</td>
<td>0.59</td>
<td>0.87%</td>
<td>104</td>
</tr>
</tbody>
</table>

**6.2 Donor-$\pi$-Acceptor Purines**

2-Aminopurine (2-AP), an isomer of adenine, remains perhaps the simplest functional nucleobase variant that is also fluorescent; a high quantum yield (68% in water for the riboside\textsuperscript{196}) underlies its widespread usage as an optical probe\textsuperscript{197} and continued mechanistic and structural study.\textsuperscript{198-200} Even so, molecules based on this platform have sparsely filtered into traditional organic materials and related sensing applications,\textsuperscript{201,202} and in surprisingly few cases has their optimization and broader photophysical evaluation toward this goal been performed.\textsuperscript{203}
Figure 6-1. Generic structure of the donor-acceptor purines (D = donor, A = acceptor). Atoms have been numbered in the conventional way around the purine core.

The organic framework considered here is that of the donor-π-acceptor purine, a heterocycle central to DNA/RNA structure that can be made highly fluorescent upon the judicious placement of electron donor and acceptor groups on its rings,\textsuperscript{203,204} as shown in Figure 6-1. Significant photophysical changes occur upon introduction of acceptor substituents to the purine C(8) position that complement typical donor groups at C(2) and C(6) positions. Recently prepared derivatives have displayed fluorescence quantum yields over 80% and emission wavelengths that can be tuned from 350 to 450 nm in solution,\textsuperscript{203,204} suitable starting parameters for blue-violet OLED construction. The interest in using purines for electronic device development is further derived from their rich chemical structure that underlies molecular recognition and charge transport\textsuperscript{205} processes in natural systems. The molecules' extended π-surface tends to facilitate aromatic stacking and can allow access to different hydrogen-bonding patterns along their heteroatom-lined edges.\textsuperscript{206} These structural features have already been shown important to the ordering of simple nucleobases in the solid state,\textsuperscript{207} where they are relevant to device performance.\textsuperscript{208,209} Hardly considered to date have been emissive purine analogs in solid-state devices, such as OLEDs.

As a first example, efficient blue-violet emitting OLEDs based on one type of donor-acceptor purine, methyl-9-benzyl-2-N,N′-dimethylamino-9H-purine-8-carboxylate
1 (Figure 6-1), are first demonstrated in this chapter. A maximum EQE of 3.1% is achieved in devices with the purine emitter dispersed in a \(N,N’\)-dicarbazolyl3,5-benzene (mCP) host matrix as the emissive layer. The electroluminescence (EL) of the OLED has a peak emission wavelength of \(\lambda = 430\) nm.

Another donor-acceptor purine derivative, methyl-2-amino-9-benzly-6-(dimethylamino)-9\(H\)-purine-8-carboxylate 2 (Figure 6-1), which has even shorter PL emission peak wavelength below 400 nm, is also used for OLEDs device demonstration. Different from the visible light and near-IR emitting materials, the blue-violet-UV emitting materials usually have very wide energy band gap (>2.6 eV), so it is very important to find out the appropriate organic materials for multilayer in devices including hole transporting layers (HTLs) or electron blocking layers (EBL), emissive layers (EMLs) and electron transporting layers (ETLs) or hole blocking layers (HBLs), to well align the energy levels between different layers in the devices when the emitters are incorporated. Emission from single layers such as HTLs or exciplex emissions from interfaces between organic layers may be observed if the electrons or holes, respectively, are not effectively injected and confined within the EMLs. These issues indicate the importance of choosing the appropriate organic materials for a multilayer OLEDs, in order to obtain the desired EL emission and high efficiencies. Based on the UV emitter, Purine 2, we study the effect of device structures by utilizing different HTLs, ETLs, EMLs and insertion of thin buffer layer to the devices for the extraction of violet-to-UV emission from OLEDs. By using the optimized device structure with appropriate energy level alignment among multilayers, a maximum EQE of 1.5% is achieved in the devices with a peak emission wavelength below 400 nm, at \(\lambda = 393\) nm.
This chapter is organized as follows. The experimental details on optical characterization, electrochemistry, device fabrication and characterization are described in section 6-3. We present the experimental results and discussion on the optical properties and performance of the OLEDs for Purine 1 in section 6-4. In section 6-5, we study the effect of device structure by utilizing different HTLs, ETLs, EMLs and insertion of thin buffer layer, for achieving the short wavelength emitting OLEDs based on purine 2. Finally, we conclude in section 6-6.

Table 6-2. Photophysical data (absorption and emission maxima, \(\lambda_{\text{max}}^\text{abs}\) and \(\lambda_{\text{max}}^\text{em}\), and quantum yields, \(\phi_{\text{em}}\)) for purine 1 and 2 measured in CH\(_2\)Cl\(_2\).

<table>
<thead>
<tr>
<th>Purine</th>
<th>(\lambda_{\text{max}}^\text{abs}) (nm)</th>
<th>(\log \varepsilon) (M(^{-1})cm(^{-1}))</th>
<th>(\phi_{\text{em}})</th>
<th>(\lambda_{\text{max}}^\text{em}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>362</td>
<td>4.1</td>
<td>0.81</td>
<td>433</td>
</tr>
<tr>
<td>2</td>
<td>330</td>
<td>4.2</td>
<td>&gt;0.95</td>
<td>393</td>
</tr>
</tbody>
</table>

6.3 Experimental Details

The synthesis of purine 1 and 2 has been reported previously.\(^{203}\) The purine molecules used in this work are synthesized by Pamela Cohn in Dr. Ronald Castellano group in the Department of Chemistry at the University of Florida. The photophysical data including the absorption and emission maxima and quantum yields in solution, for these two purines, are listed in Table 6-2.

Solution steady-state fluorescence emission spectra were recorded on a SPEX Fluoromax spectrophotometer. The optical density was less than 0.1, and the sample concentration ranged from 5-10 \(\mu\)M. Solid-state films were prepared by vacuum thermal evaporation on quartz substrates. Photoluminescence spectra for the films were obtained choosing certain excitation wavelengths that usually corresponded to the absorption maxima of test materials as recorded with a JASCO FP-6500 spectrofluorometer.
Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) measurements were performed in an Ar-atmosphere glovebox maintained with < 4 ppm trace oxygen and moisture. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was purchased from Aldrich and used as received. Dichloromethane (DCM) was passed through a MBraun solvent purification system that renders the solvent dry on retrieval. The purine solid was dissolved to a concentration of 4.5 mM in a 0.1 M TBAPF$_6$/DCM electrolyte. The working reference, and counter electrodes were a Pt button (0.02 cm$^2$), a silver wire pseudoreference calibrated with the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple, and a platinum flag, respectively.

The above PL spectra of purine molecules in solution and CV/DPV characterization are measured by Aubrey Dyer in Dr. John Reynolds group in the Department of Chemistry at the University of Florida.

The multilayer OLEDs were fabricated on glass substrates commercially precoated with an indium tin oxide (ITO) anode with a sheet resistance of ~ 20 $\Omega/\square$. The substrates were cleaned and processed by the standard procedure described in previous chapters. All the layers, including the cathode, were deposited using vacuum thermal evaporation following procedures published previously.$^{39}$ The organic layers in the device structure usually consist of hole transporting layers (HTLs), emissive layer and electron transporting layers (ETLs) in sequent. The HTLs used in this chapter include 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), 4,4’,4”-tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine (m-MTDATA), 4,4’,4”-tris(carbazol-9-yl)triphenylamine (TcTa), and $\alpha$-NPD. mCP is used as the host material. For some devices, neat emitter layers are directly used, sandwiched by HTL and ETL layers,
without mixing into the host matrix. The ETLs used include 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene (OXD-7), 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi), 3-(4-biphenylyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole (TAZ), BPhen, and 3TPYMB. The thickness of the HTL and ETL were both 40 nm, whereas the EML was 20 nm consisting of either the mCP host doped with emitters at different doping concentrations or the neat emitter layers. A 5 nm thick $p$-bis(triphenylsilyl)benzene (UGH2)$^{37}$ is inserted between host and ETLs in some devices as the buffer layer. A 1 nm thick layer of LiF followed by a 50 nm Al layer was then deposited as the cathode.

The deposition rates for the organic layers were 0.1–0.2 nm/s, as monitored by quartz crystal microbalances. The active device area was 4 mm$^2$ with the electrodes arranged in a cross-bar geometry, and each substrate featured four independently addressable device pixels. TAPC, m-MTDATA, TcTa, mCP, OXD-7, TPBi, TAZ, 3TPYMB and UGH2 were all purchased from Luminescence Technology Corp, BPhen from TCI America, and α-NPD from e-Ray. All organic materials were used as obtained except for α-NPD and BPhen, which were purified in house using vacuum gradient sublimation method for one to two cycles.$^{14}$ The HOMO/LUMO energies for all the materials above are taken from the literature,$^{39,43,108,211,212}$ whereas the HOMO/LUMO energies for the purines are determined experimentally using CV and DPV.

Radiant emittance ($R$)–current density ($J$)–voltage ($V$) characteristics of the OLEDs were measured under ambient conditions using an Agilent 4155C semiconductor parameter analyzer and a calibrated silicon detector (Newport 818 UV). EL spectra and the Commission Internationale de L’Eclairage (CIE) coordinates were
taken using an OceanOptics HR4000 spectrometer with the devices driven at a constant current using a Keithley 2400 source meter. The radiant emittance was calibrated assuming Lambertian emission, and the EQE ($\eta_{EQE}$) and “wall plug” power efficiency ($\eta_P$) were derived based on the recommended methods. The organic layer thickness nonuniformity across the samples and run-to-run variations typically lead to 5–10% error in device efficiencies.

6.4 Blue-Violet OLEDs based on Purine 1

Figure 6-2 shows the photoluminescence (PL) spectra of 1 in solid-state film with 5% doping concentration in mCP. The films are prepared by vacuum thermal evaporation on quartz substrates and the film thickness is 20 nm. Independent PL spectra for the films were obtained using excitation wavelengths that correspond to the absorption maxima of mCP ($\lambda_{ex} = 292$ nm) and purine 1 ($\lambda_{ex} = 362$ nm). Compared to the PL spectra of neat mCP film excited at $\lambda_{ex} = 292$ nm shown in Figure 6-2, the purine 1 doped mCP film shows the red-shifted emission peak at $\lambda_{em} = 432$ nm when also excited at 292 nm, which can be attributed to the emission from purine 1. This result indicates that Förster energy transfer$^{114}$ of excitons occurs from the mCP host to the purine dopant molecules. It can be further proved by the PL spectra of the same doped film excited at $\lambda_{ex} = 362$ nm, a wavelength at which purine 1 has maximum but mCP has negligible absorption. The PL emission of doped film excited at the absorption maximum of purine 1, in spite of the lower intensity due to low composition of purine 1 in the film, is identical to that excited at the absorption maximum of mCP, as shown in the inset of Figure 6-2. Additionally, the PL spectra of purine 1 in solution and the solid state show identical emission maxima ($\lambda_{em} = 432$ nm) suggesting that the purine molecules are
well-dispersed in the mCP host matrix and do not exhibit aggregation-induced red-shifted emission.

Figure 6-2. Photoluminescence spectra of purine 1 in solid-state film (5 wt% in mCP) when excited at $\lambda_{ex} = 292$ nm (solid line) and 362 nm (dashed line). PL spectrum of mCP film (excited at $\lambda_{ex} = 292$ nm) is also shown for comparison. Inset: The molecular structure of purine 1 and normalized PL spectra of purine in solid-state films (5 wt% in mCP) when excited at $\lambda_{ex} = 292$ nm (solid line) and 362 nm (dashed line). PL spectrum of purine 1 in CH$_2$Cl$_2$ solution (dashed-dotted line; $\lambda_{ex} = 320$ nm) is also shown for comparison.

Most encouraging is that while the PL quantum yield for purine 1 in organic solution (81% in CH$_2$Cl$_2$, Table 1) is high relative to violet emitters reported previously,$^{101,104,106}$ it is not the highest reported for donor-acceptor purines.$^{203}$ Likewise, it is known that small changes to the donor and acceptor groups of purine 1 can tune its emission across the blue-UV region,$^{203}$ potentially suitable for a variety of OLED applications.

The energies of the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) for purine 1 were determined experimentally using
cyclic voltammetry (CV) and differential pulse voltammetry (DPV). This knowledge has guided the choice of charge transport and injection layers for proper energy level alignment with the active material to maximize OLED efficiency. The E$_{1/2}$ for oxidation and reduction (vs. Fc/Fc$^+$) were measured as 0.97 V and -2.24 V, respectively. The HOMO and LUMO energy values were then calculated from the electrochemical data as 6.07 and 2.86 eV, respectively, considering that Fc/Fc$^+$ = 5.1 eV relative to vacuum.$^{213}$ The corresponding HOMO-LUMO gap energy (3.2 eV) lies between those reported previously$^{203}$ from optical absorption data (3.0 eV) and electronic structure calculations (3.88 eV at the B3LYP/6-311++G** level).

Figure 6-3. (color) Schematic energy level diagram of the OLEDs using purine 1 as the emitter with different ETLs. The energies (in eV) for the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) of the organic materials and the Fermi levels of the electrodes are referred from the vacuum level. The dashed lines in the mCP layer correspond to the LUMO and HOMO levels of purine 1.

The schematic energy level diagram of the multilayer OLED structure based on purine 1 is shown in Figure 6-3. We first study the effect of different ETLs on the OLEDs based on purine 1. With a constant 3% doping concentration in mCP, the ETLs with the thickness of 40 nm are varied from OXD-7, 3TPYMB to BPhen.$^{43,214}$
Figure 6-4. (color) A) Normalized electroluminescence (EL) spectra of the purine 1 based OLEDs with OXD-7 (red), 3TPYMB (blue), and BPhen (green) as ETLs. B) Current density, \( J \), and radiant emittance in the forward viewing directions, \( R \), as functions of voltage, \( V \), for these three devices. C) External quantum efficiency, \( \eta_{EQE} \), and power efficiency, \( \eta_P \), as functions of current density, \( J \), for these three devices.
The EL spectra of these three devices show almost the same emission peaked at approximately 430 nm, as shown in Figure 6-4A, consistent with the PL emission in both solution and solid-state films. The current density and radiant emittance of these devices are shown in Figure 6-4B. The current densities of devices decrease from BPhe to 3TPYMB and to OXD-7,\textsuperscript{43,214} which can be attributed to the decreasing conductivity of these three ETL materials. Accordingly, the radiant emittances of these three devices follow the same trend as current densities. But a maximum radiant emittance is achieved by OLEDs with the least conductive OXD-7, due to the higher saturation voltage of the OXD-7 device compared to the other two devices. Here, the actual optical power density of the OLED emission is reported instead of the more commonly used luminance, as the latter incorporates the human eye sensitivity and is intended for display and lighting applications. Moreover, the luminance value of the OLED is dominated by the longer wavelength (blue and green) components in the emission spectrum, and does not clearly present the contributions from the shorter wavelength (UV to violet) emissions, the focus of this work. The OXD-7 device also shows the highest EQE among these three devices as shown in Figure 6-4C. This is probably due to the lower electron injection barrier for host/ETL interface (Figure 6-3) and optimal charge balance within the device when using OXD-7 as the ETL.\textsuperscript{215} Therefore, in the following work we will use OXD-7 as ETL for further device performance optimization.

The OXD-7 ETL layer thickness is then optimized considering the further charge balance optimization and microcavity effect as mentioned in the previous chapters. As the thickness of OXD-7 increases from 30 to 40 nm, both the EQE and power
efficiencies are improved, while further increase of the thickness to 50 nm will lead to the decrease of device efficiencies, as shown in Figure 6-5. Therefore, the optimal OXD-7 thickness in the devices is determined to be 40 nm.

Figure 6-5. (color) External quantum efficiency, $\eta_{\text{EQE}}$, and power efficiency, $\eta_P$, as functions of current density, $J$, for the purine 1 based devices with various OXD-7 ETL layer thicknesses.

Figure 6-6. Maximum external quantum efficiency, $\eta_{\text{EQE}}$, and power efficiency, $\eta_P$, of OLEDs (with 40 nm thickness of OXD-7 ETL) as functions of the doping concentration, $x$, of purine 1.
The maximum EQE and power efficiencies of OLEDs with various doping concentrations of purine 1 in the mCP host matrix are shown in Figure 6-6. The OXD-7 thickness in these devices is maintained at 40 nm. Both the EQE and power efficiency curves show the same trend; i.e., the efficiencies increase with doping concentration of purine 1 for 1%<x<4%, and then decrease with further increase of x to 6%. So the doping concentration of purine 1 in OLEDs is optimized as 4%.

Figure 6-7. External quantum efficiency, \( \eta_{\text{EQE}} \), of the optimal purine 1 based OLED as a function of the current density, \( J \). Inset: Current density, \( J \), and the radiant emittance, \( R \), as functions of the voltage, \( V \), for this device.

Current density-voltage (\( J-V \)) and radiant emittance-voltage (\( R-V \)) characteristics of an OLED based on purine 1 with optimized purine 1 doping concentration of 4% and OXD-7 ETL thickness of 40 nm, are shown in the set of Figure 6-7. The turn-on voltage of this device, which is defined as the operating voltage that yields detectable light emission (in this case it means \( R > 10^{-5} \) mW/cm\(^2\)), is approximately \( V_T = 2.9 \pm 0.1 \) V. Note that the photon energy corresponding to the peak emission (\( \lambda_{\text{em}} = 432 \) nm) is 2.9 eV. This suggests that there is negligible energy loss to induce the EL from purine in
this OLED device architecture. The light output increases drastically with the operating voltage at $V > V_T$, and a radiant emittance in the range of 10 to 18 mW/cm$^2$ is achieved at $V > 15$ V. Figure 6-7 shows the dependency of $\eta_{\text{EQE}}$ on the current density. The device has a maximum EQE of $(3.1 \pm 0.3)\%$, a value that approaches the highest efficiency OLEDs with peak emission approaching 440 nm.$^{16-18}$ The power efficiency for the device reaches a maximum of $(23 \pm 3)$ mW/W at low current densities $(10^{-3} < J < 10^{-2}$ mA/cm$^2$), and is reduced to $(13 \pm 2)$ mW/W at $J = 1$ mA/cm$^2$ mostly due to the increase in operating voltage.

Figure 6-8. Normalized EL spectrum for the OLED based on purine 1 at $J = 1$ mA/cm$^2$. Inset: Device picture with four pixels in one substrate all lighten up.

As shown in Figure 6-8, the EL spectrum of the device measured at $J = 1$ mA/cm$^2$ reveals peak emission at $\lambda = 430$ nm with a full width at half maximum of 60 nm, nearly identical to the PL emission obtained in solid-state films. The Commission Internationale de L’Eclairage (CIE) coordinates of this OLED are (0.15, 0.06). The emission peak of $\lambda = 430$ nm falls into the violet spectral range (380-450 nm); however, we do recognize that the emission from these OLEDs does contain a significant blue component (440-490 nm) and even longer wavelengths. As a result, we define the electroluminescence
from the purine-based OLEDs as blue-violet emission. Considering that the human eye has a much higher photopic response to blue (and even higher to green) than to violet light, overall the emission of these purine-based OLEDs appears to be blue to our eyes, as shown by the device picture in the inset of Figure 6-8.

![Graph](image)

**Figure 6-9.** (color) Electroluminescence intensity decay of optimal purine-based OLEDs driven at a constant current density of 1 mA/cm² in air. The operational voltage change with the constant current density is also shown.

The operational stability of the purine-based OLEDs is also tested in air by measuring the electroluminescence intensity decay of the OLEDs driven at a constant current density of 1 mA/cm². As shown in Figure 6-9, the device shows a half-intensity lifetime of about 500 seconds, but the decay appears to slow down after an initial burn-in period. For example, from 200 seconds to 1200 seconds (an interval of 1000 seconds), the EL intensity is reduced by approximately 50%. The relatively low device lifetime may be due to the chemical stability of the purine, and we also believe that potentially useful device lifetimes should be achievable if we employ good encapsulation for these devices and/or optimization of device structure as has been accomplished in the commercial sector for visible light emitting OLEDs. The operational
voltages are also gradually increased with the device operation time, from the initial
ing voltage of 7.2 V to 7.6 V after 20 min continuous operation, probably due to the
degradation of devices.

6.5 Violet-UV Emitting OLEDs based on Purine 2

With different donor groups connected to the heterocycle ring, another donor-
acceptor purine 2 exhibits further shorter emission wavelength peaked at 393 nm and
very high quantum yield close to unity in the solution (Table 6-1). Figure 6-10 shows the
photoluminescence (PL) spectra of 2 in solid-state films (as a dispersion in mCP or neat
film). Doped solid-state films were prepared by vacuum thermal evaporation and
consisted of a 20 nm thick mCP layer doped with 5% (by weight) purine 2. Independent
PL spectra for the films were obtained using excitation wavelengths that correspond to
the absorption maxima of mCP ($\lambda_{ex} = 292$ nm) and purine 2 ($\lambda_{ex} = 330$ nm).

![Photoluminescence spectra of purine 2](image)

Figure 6-10. Photoluminescence spectra of purine 2 in solid-state films with 5 wt% in
mCP when excited at $\lambda_{ex} = 292$ nm (solid line) and 330 nm (dashed line), and
neat purine 2 film excited at $\lambda_{ex} = 330$ nm (dashed-dotted line). Inset: The
molecular structure of purine 2.
The PL spectra for these doped films show identical emission maxima with that in the solution ($\lambda_{em} = 393$ nm), suggesting that the purine molecules are well-dispersed in the mCP host matrix and do not exhibit aggregation-induced red-shifted emission. Additionally, the two doped solid-state film shows the same PL emission ($\lambda_{em} = 393$ nm) whether excited at the absorption maximum of mCP ($\lambda_{ex} = 292$ nm) or the absorption maximum of purine 2 ($\lambda_{ex} = 330$ nm, a wavelength at which mCP has barely absorption). This result indicates that Förster energy transfer$^{114}$ of excitons occurs from the mCP host to the purine dopant molecules.

But for the solid-state film with neat purine 2, a significant red shift over 70 nm relative to the solution PL emission peak has been observed, which indicates that the purine 2 have very strong inter-molecular interaction, leading to aggregation-induced red-shifted emission.

![EL spectrum](image)

Figure 6-11. (color) EL spectrum for the OLEDs based on neat purine 2 as EML, measured at various current densities from $J = 10$ mA/cm$^2$ to 375 mA/cm$^2$.

The OLEDs using a 20 nm thick neat purine 2 as the EML show similar emission with solid-state films, both with largely red-shifted emission peak wavelengths at 470
nm, as shown in Figure 6-11. The devices have TAPC and BPhen as HTL and ETL, respectively, both with thickness of 40 nm. The emission of this device obviously falls into the range of blue emission, instead of violet as predicted by the solution PL data.

As suggested by PL emission of both doped and neat solid-state films, the purine 2 must be dispersed into host matrix in the devices to prevent the aggregation-induced red-shifted emission. We still use mCP as host material doped with 5% purine 2 molecules as EML for the OLEDs, as the previous film PL emission results have shown efficient Förster energy transfer of excitons from the mCP host to the purine dopant molecules (Figure 6-10).

![Normalized EL spectra for the OLEDs based on purine 2 doped EML (doped device, solid) and neat mCP EML (control, dashed). HTL and ETL for these devices are TAPC and BPhen, respectively.](image)

The combinations of a series of HTL/ETL materials, including TAPC/BPhen, TAPC/TAZ, TAPC/OXD-7, TAPC/3TPYMB, NPB/BPhen, m-MTDATA/BPhen and PEDOT:PSS/OXD-7 are used for the OLEDs with doped EML. Unfortunately, no emission of purine 2 has been observed for all those devices. For example, the EL spectra of the OLEDs with TAPC and BPhen as HTL and ETL, respectively, are shown.
in Figure 6-12. The control device, which contains only neat mCP in the EML without purine, is also made for comparison. The doped EML device shows almost the same spectra as the control device, both with emission peak wavelengths of 410 nm, suggesting there is no contribution of emission from purine 2 molecules for the device with purine 2 doped EML. This same emission from both doped and control devices can be attributed to the exciplex emission\[^{216-218}\] at the interfaces of EML and ETLs.

The exciplex emissions at the interfaces are also observed when other ETL materials are used, with peak wavelengths of approximately 400-410 nm, as shown in Figure 6-13. The energy differences at mCP/ETL interfaces, which are the energy gaps between the HOMO level of mCP and LUMO levels of ETLs, can be calculated of approximately 2.9 eV, 3.1 eV, and 3.2 eV for BPhen, OXD-7 and TAZ based devices, respectively (Figure 6-3). So the exciplex emissions at the interfaces will then gradually blue-shift from BPhen to OXD-7, and TAZ based devices, which is in good agreement with the trend shown in Figure 6-13.

![Normalized EL spectra for the OLEDs based on purine 2 doped EML with different ETLs (ETLs = BPhen, OXD-7 and TAZ). TAPC is used as the HTL for these devices. The spectra are only shown for the range of 330 – 530 nm for better comparison of peak shift.](image)

Figure 6-13. (color) Normalized EL spectra for the OLEDs based on purine 2 doped EML with different ETLs (ETLs = BPhen, OXD-7 and TAZ). TAPC is used as the HTL for these devices. The spectra are only shown for the range of 330 – 530 nm for better comparison of peak shift.
Another possible emission path is the exciton emission of HTL layers, as shown in Figure 6-14, for OLEDs with doped EML and BPhen as ETL. The similar emissions peaked at 430-440 nm for both α-NPD and m-MTDATA based devices are due to the emission from the corresponding HTLs,\textsuperscript{219,220} while TAPC based devices do not show this emission. The layer of α-NPD has 0.4 eV lower LUMO level than TAPC, as shown in Figure 6-15, and there is almost no energy barrier for the electron injection from mCP host to α-NPD. So the relatively large amount of injected electrons in α-NPD recombines with holes in α-NPD, giving out the emission of α-NPD. For m-MTDATA based devices, the hole injection barrier from m-MTDATA to mCP host is much larger than the TAPC based devices, while the electron injections from host to HTL are almost the same for both devices (Figure 6-15). So the holes are continuously injected and accumulate in the layer of m-MTDATA due to the high energy barrier at HTL/host interface. These accumulated holes then have greater chances to recombine with the injected electrons in m-MTDATA layer and lead to the emission of m-MTDATA. The tail
emission extended to as far as 600 nm in both α-NPD and m-MTDATA based devices can be probably attributed to the exciplex emission at the HTL/host interface.

Figure 6-15. (color) Schematic energy level diagram of the OLEDs using purine 2 as the emitter with different HTLs (HTLs = TAPC, α-NPD and m-MTDATA). The HOMO and LUMO of purine 2 are not indicated here.

The exciton formation is usually more favorable when the electrons and holes binded with lower energy. In the above purine 2 based devices, due to its high energy band gap which corresponds to the emission peak of 393 nm, the formations of exciplex at host/ETL interfaces (corresponding to the emission peak over 400 nm) and excitons of HTLs (corresponding to the emission peak at 430-440 nm) are then more favorable compared to the formation of excitons of purine 2, for the variable ETLs and HTLs devices, respectively. As a result, the devices will emit through the recombination of these favorable states instead of the purine 2 excited states. These results above suggest the importance of appropriate energy level alignment in the multilayer OLEDs with large band gap molecules as emitter. All the functional layers, including hole and electron transporting layers and host matrix, need to be carefully chosen to facilitate the formation of stable excited states of emitter molecules, and at the same time avoid other possible competitive emission paths.
Figure 6-16. (color) Normalized EL spectra for the OLEDs based on purine 2 doped EML (doped device, red solid line) and neat mCP EML (control, black solid line) with the insertion of thin layer of UGH2. HTL and ETL for these devices are TAPC and OXD-7, respectively. The PL emission of purine 2 doped mCP film (black dashed line) is also shown for comparison. Inset: the schematic energy level diagram of the purine 2 doped device. The HOMO and LUMO of purine 2 are not indicated.

Based on the above discussion, TAPC is eligible for the hole transporting layer since no HTL emission is observed for all TAPC based devices (Figure 6-13). To prevent the exciplex emission at the EML/ETLs interfaces, a thin layer of UGH2 (5 nm) with very wide band gap is inserted between the host and ETLs (OXD-7). mCP is still used as the host material doped with 5% purine 2. Figure 6-16 shows the EL spectrum of this device as well as the control device with only neat mCP in the EML and the PL emission of purine 2 doped mCP film for comparison. After the insertion of UGH2 thin layer, the
OLEDs based on purine 2 show very similar emissions with the PL emission of purine 2 doped film, both with emission peak at 393 nm. This result strongly indicates that the purine 2 emission is achieved by the device with UGH2 thin layer. Comparatively, the control device shows relatively blue-shifted and very noisy emission and an additional peak at approximately 580 nm with an intensity of 15% of that of the primary peak.

Figure 6-17. (color) A) Current density, $J$, and the radiant emittance, $R$, as functions of the voltage, $V$, for the OLEDs based on purine 2 doped EML (doped device, red triangles) and neat mCP EML (control, blue squares) with the insertion of thin layer of UGH2. B) External quantum efficiency, $\eta_{\text{EQE}}$, of these two OLEDs as a function of the current density, $J$.

One more evidence for successfully obtaining the purine 2 emission in OLEDs with UGH2 thin layer is the comparison of radiant emittance ($R$)-current density ($J$)-voltage ($V$) characteristics and device efficiencies between the doped and control
devices, as shown in Figure 6-17. These two devices show completely different $R$-$J$-$V$ characteristics including the different turn-on voltages, and different orders of magnitude of current densities and radiant emittances. The EQE of doped device is also two times higher than the control device. All these differences suggest that the doped and control devices have completely different emission manners within the devices, therefore leading to the different EL emission spectra as shown in Figure 6-16. The small amount of doped purine 2 (5% by weight) may only slightly affect the current densities and radiant emittances if these two devices have the same emission mechanism, and the EQE should be not significantly different between the two devices, which are obviously not the case as shown in Figure 6-17. The largely enhanced current density, radiant emittance and device efficiency indicate the doped device has a robust emission mechanism, which is greatly likely to be the Förster energy transfer from the host to purine molecules.

The purine 2 based OLEDs, which employ the device structure of ITO/TAPC/mCP:5%Purine 2/UGH2/OXD-7/LiF/Al, have a maximum EQE of $\eta_{\text{EQE}} = (1.5 \pm 0.2)\%$ achieved at $J \approx 1$ mA/cm$^2$, and a maximum radiant emittance of 5 mW/cm$^2$ at $V = 17$ V, as shown in Figure 6-17. The efficiency of purine 2 based OLEDs is two times lower than the purine 1 devices but the former devices shift the emission further towards the short wavelength range with the emission peak below 400 nm, at $\lambda = 393$ nm.

6.6 Summary

In this chapter, firstly, a blue-violet electroluminescent device has been constructed featuring a highly fluorescent donor-acceptor purine 1 in the emissive layer. Its defining parameters, a maximum external quantum efficiency of 3.1%, a turn-on
voltage of 2.9 V, and peak emission at 430 nm, are achieved by optimizing the doping concentration of purine in host matrix, and materials and thickness of electron transporting layer. These results are comparable to state-of-the-art UV to violet emitting OLEDs and approach the highest performing deep-blue OLEDs based on fluorescent organic compounds.

With different donor groups connected to the purine heterocycle ring, another donor-acceptor purine derivative 2, which exhibits further blue-shifted emission with peak wavelength below 400 nm and very high quantum yield close to unity in the solution, is also employed for violet-UV emitting OLEDs. Due to the high energy band gap of purine 2 molecules, it is very important to appropriately align the energy levels of different layers in the multilayer devices to efficiently extract the desired light emission. So we study the effect of device structures by utilizing different HTLs, ETLs, EMLs and insertion of thin buffer layer for purine 2 based OLEDs. By using the optimized device structure with appropriate energy level alignment among multilayer, the purine 2 based devices have a maximum external quantum efficiency (EQE) of 1.5%, two times lower than the purine 1 based devices, but the purine 2 based devices further shift the emission towards the short wavelength range with emission peak wavelength below 400 nm, very close to the real UV emission.

Central to the purine-based emissive component is a rich (and highly modifiable) chemical structure that is linked to broad functions in biology and emerging applications in materials science.\textsuperscript{221,222} Given that extension of the donor-acceptor concept to the purine heterocycle has allowed highly efficient and tunable fluorescence emission across the blue-UV spectrum in solution, the results reported here bode well for
continued OLED development using the molecules to design devices with tailored
electroluminescence. The extent to which the molecular recognition functionality of the
purine (e.g., hydrogen bonding sites) can be used to modulate the EML and interface
structure toward improved device performance will be a focal point of future studies.

As the emission of OLEDs goes to the even shorter wavelength range, it is more
and more difficult to find out the appropriate organic materials for different functional
layers such as HTLs, ETLs, EMLs and buffer layers to achieve energy level alignment
for multilayer, since so far, most of available organic materials are designed for the use
of OLEDs emitting visible light, which corresponds to the relatively small energy band
gaps compared to the UV emitters. So organic materials as use of the functional layers
in violet-UV OLEDs with specific requirements, such as larger energy band gap,
reasonable HOMO/LUMO levels, and good electrical properties, need to be designed
and synthesized in the future.
CHAPTER 7
CONCLUSIONS AND FUTURE WORKS

7.1 Conclusions

7.1.1 Near-IR OLEDs based on Fluorescent Donor-Acceptor-Donor Oligomers

In Chapter 4, we demonstrate that low-gap DAD oligomers are good candidate materials for use in OLEDs to achieve efficient NIR emission. A maximum external quantum efficiency of 1.6% and a maximum power efficiency of 7.0 mW/W were achieved in devices based on BEDOT-TQMe$_2$, whose emission peaks at 692 nm, but extends to well above 800 nm. With a stronger acceptor and thus a reduced energy gap, longer wavelength NIR emissions peaked at 815 nm were achieved in BEDOT-BBT based devices, although the efficiencies were approximately three times lower than the BEDOT-TQMe$_2$ based devices, due to the significantly lower fluorescent quantum yield of BEDOT-BBT.$^{185}$ Using the sensitized fluorescence device structure,$^{154}$ the efficiencies were further increased by two to three times, and we achieved the maximum efficiencies of $\eta_{\text{EQE}} = 3.1\%$ and $\eta_{\text{P}} = 12 \text{ mW/W}$ for BEDOT-TQMe$_2$ based devices, and $\eta_{\text{EQE}} = 1.5\%$ and $\eta_{\text{P}} = 4.0 \text{ mW/W}$ for BEDOT-BBT based devices.$^{186}$

The aggregate effect of the donor-acceptor-donor oligomers in the devices is also studied by utilizing different host matrix and changing the stacking manners of doping molecules. Changing from the previous host of Alq$_3$ to CBP, which has more spectral overlap with the DAD NIR emitters, the concentration of NIR emitters needed to allow complete energy transfer for excitons on the host molecules will be decreased due to increased Förster radius, leading to less significant aggregate quenching effect. The NIR OLEDs based on BEDOT-BBT doped into CBP host matrix has a maximum EQE of $\eta_{\text{EQE}} = (0.92 \pm 0.07)\%$, which is almost double that of the devices with Alq$_3$ as host. The
power efficiency is also higher for the CBP device than the device with Alq3 host, with a maximum of $\eta_P = (3.6 \pm 0.3)$ mW/W for the former device. The effect of molecular structure on aggregation in devices is then studied by adding bulky substituted groups to the two ends of DAD oligomers. However, the NIR OLEDs based on two bulky DAD oligomers show similar aggregate effect, compared to “bare” BEDOT-BBT based devices. The efficiencies of these bulky DAD oligomers based devices show no enhancement and the emissions are red-shifted with peak wavelengths up to 905 nm.

**7.1.2 Near-IR OLEDs based on Phosphorescent Platinum (II) Porphyrins**

In Chapter 5, we have demonstrated the incorporation of a family of π-extended Pt-porphyrins, including the novel Pt-Ar$_4$TAP derivative, into NIR OLEDs. Through the extension of the π-system to Pt-Ar$_4$TAP the electroluminescence was shifted to 1005 nm, which is the longest wavelength demonstrated to date for a triplet phosphor in an electroluminescent device. The photophysical and OLED data on this series of π-extended Pt-porphyrins were compared, revealing decreasing solution $\phi_{em}$ and device efficiency as the π-system is extended and the emission is bathochromically shifted from ~770 nm to ~1005 nm.

The photophysics of a series of variously substituted Pt-tetrabenzoporphyrins were characterized both in solution and solid state and compared with their performance in OLEDs. Although relatively large differences in $\phi_{em}$ and $\tau_{em}$ between di- and tetra-substituted Pt-TBPs were observed in solution, the difference in $\tau_{em}$ was barely found in host matrix of devices. The results of this study clearly demonstrate that the large differences observed for the solution $\phi_{em}$ do not directly correlate with the performance of the chromophores in devices. It was also found that the addition of 3,5-di-tert-
butylphenyl groups in place of phenyl groups on the benzoporphyrin ring periphery results in increased device efficiency; however, further increasing the size of the substituents to bulkier groups (such as terphenyl) does not improve the device performance. Although the efficiency improvements obtained with the di-substituted Pt-benzoporphyrins were not as high as predicted by their solution $\phi_{em}$ values, the NIR OLEDs based on the series of di-substituted Pt-TBPs still achieve very high efficiencies with maximum EQE up to 7-8% in the near-IR emission range. A record high EQEs were finally obtained by OLEDs based on Pt-Ar$_4$TBP emitting at the peak wavelength of 773 nm with EQE of 9.2%.$^{189}$

Finally, the aggregate effect of Pt-TBPs on EL efficiency is studied based on the two Pt-porphyrin molecules: Pt-Ar$_4$TBP, which has bulky end groups added in place of the meso-aryl groups on the benzoporphyrin ring periphery, and the non-substituted counterpart, Pt-TPTBP. By comparing the efficiency decay rate with the increasing doping concentration of the two emitters, we find that the bulkier Pt-Ar$_4$TBP exhibits much less significant aggregate than Pt-TPTBP in the devices.

7.1.3 Ultra-Violet Organic Light Emitting Devices

In Chapter 6, a blue-violet electroluminescent device has been constructed featuring a highly fluorescent donor-acceptor purine in the emissive layer.$^{210}$ Its defining parameters, a maximum EQE of 3.1%, a turn-on voltage of 2.9 V, and peak emission at 430 nm, are comparable to state-of-the-art UV to violet emitting OLEDs and approach the highest performing deep-blue OLEDs based on fluorescent organic compounds.

With different donor groups connected to the purine heterocycle ring, another donor-acceptor purine derivative 2, which exhibits further blue-shifted emission with
peak wavelength below 400 nm and very high quantum yield close to unity in the solution, is also employed for violet-UV emitting OLEDs. Due to the high energy band gap of purine 2 molecules, it is very important to appropriately align the energy levels of different layers in the multilayer devices to efficiently extract the desired light emission. So we study the effect of device structures by utilizing different HTLs, ETLs, EMLs and insertion of thin buffer layer for purine 2 based OLEDs. By using the optimized device structure with appropriate energy level alignment among multilayer, the purine 2 based devices have a maximum external quantum efficiency (EQE) of 1.5%, two times lower than the purine 1 based devices, but the purine 2 based devices further shift the emission towards the short wavelength range with emission peak wavelength below 400 nm, very close to the real UV emission.

Central to the purine-based emissive component is a rich (and highly modifiable) chemical structure that is linked to broad functions in biology and emerging applications in materials science. Given that extension of the donor-acceptor concept to the purine heterocycle has allowed highly efficient and tunable fluorescence emission across the blue-UV spectrum in solution, the results reported here bode well for continued OLED development using the molecules to design devices with tailored electroluminescence. The extent to which the molecular recognition functionality of the purine (e.g., hydrogen bonding sites) can be used to modulate the EML and interface structure toward improved device performance will be a focal point of future studies.

7.2 Future Works

7.2.1 Near-IR OLEDs of Longer Emission and Higher Efficiency

Already seen in this dissertation, as the energy band gaps get lower for near-IR emitting materials (including both DAD oligomers and Pt-porphyrins), the quantum
yields and lifetimes will decrease, partially due to the increased non-radiative decay rate in the lower gap molecules. This fact will, to some extent, prevent the further development of high efficiency near-IR OLEDs with even longer emission wavelength (> 1μm). Novel near-IR emitters with longer emission wavelengths but still exhibiting high quantum yield may be found out. On the other hand, another limitation for the relatively low efficiencies of these NIR OLEDs is the low light outcoupling efficiency, which is usually considered to be less than 20%. So there is still large improvement space for light outcoupling. Many methods such as the application of microlens arrays have been reported to improve the light coupling for visible light emitting OLEDs.\textsuperscript{51-54} Those same methods may be also used for NIR OLEDs. Simulation need to be done first to realize the estimated enhancement.

### 7.2.2 Application of Near-IR Emitters in OPVs

These low band gap near-IR emitting materials have the absorption in relatively longer wavelength range, which will have perfect spectra coverage with the solar spectrum.\textsuperscript{223-225} So it is possible to use these materials in the organic photovoltaic (OPV) devices and tandem OPVs.

Standard OPV devices have been tried based on the two donor-acceptor-donor oligomers, BEDOT-TQMe\textsubscript{2} and BEDOT-BBT.\textsuperscript{226} Figure 7-1 shows the J-V characteristics in the dark and under simulated AM1.5 solar illumination for a bilayer cell with the structure of ITO/BEDOT-TQMe\textsubscript{2}(200 Å)/C\textsubscript{60}(400 Å)/BCP(80 Å)/Al(800 Å). The output parameters of this cell under illumination are summarized in the inset. The low short-circuit current density ($J_{sc}$) less than 0.01 mA/cm$^2$ and fill factor (FF) of 0.20, lead to the poor device power conversion efficiency (PCE) of 0.001%, probably due to the low conductivity of BEDOT-TQMe\textsubscript{2} molecules.
Figure 7-1. (color) Current density vs voltage ($J$-$V$) characteristics of an organic photovoltaic cell with the structure of ITO/BEDOT-TQMe$_2$(200 Å)/C$_{60}$(400 Å)/BCP(80 Å)/Al(800 Å) in the dark (black) and under simulated AM 1.5G solar illumination, 1 sun (red). The device output parameters including short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$), power conversion efficiency ($PCE$) are listed in the inset.

Figure 7-2. (color) External quantum efficiency, $\eta_{EQE}$, as a function of the wavelength, for BEDOT-TQMe$_2$:C$_{60}$ bilayer cell. Inset: the schematic energy level diagram of this cell.

The external quantum efficiency of this cell, as shown in Figure 7-2, is very low, less than 1% for the whole spectrum, and shows most of the contributions from C$_{60}$. 

$$J_{sc} = 0.008 \text{ mA/cm}^2$$
$$V_{oc} = 0.66 \text{ V}$$
$$FF = 0.20$$
$$PCE = 0.001\%$$
corresponding to the peaks at about 350 nm and 440 nm. The BEDOT-TQMe$_2$ peak, which should appear at ~530 nm (Figure 4-2), can be barely seen, indicating there is very little or probably no contribution of electrical output from BEDOT-TQMe$_2$.

![Graph](image)

Figure 7-3. (color) Current density vs voltage ($J$-$V$) characteristics of an organic photovoltaic cell with the structure of ITO/BEDOT-BBT(200 Å)/C$_{60}$(400 Å)/BCP(80 Å)/Al(800 Å) in the dark (black) and under simulated AM 1.5G solar illumination (red). The device output parameters including short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$), power conversion efficiency ($PCE$) are listed in the inset.

The DAD oligomer, BEDOT-BBT, with smaller energy band gap and longer absorption wavelengths, is also used for the OPV devices. As shown in Figure 7-3, the cells based on BEDOT-BBT exhibit improved device output than the BEDOT-TQMe$_2$, with $J_{sc}$ and $PCE$ greatly enhanced to 0.19 mA/cm$^2$ and 0.02%, respectively, and $V_{oc}$ and $FF$ stay the same. The low $FF$ for both oligomers based OPV devices suggests the charge collection in these two devices is not efficient. Since BEDOT-BBT and BEDOT-TQMe$_2$ have the similar conductivities (Figure 4-9), there should be some other reasons leading to the difference of the $J_{sc}$ for these two devices. One possible explanation is that the BEDOT-BBT molecules have higher absorption coefficient and also more absorption overlap with solar spectrum.
Figure 7-4. (color) External quantum efficiency, $\eta_{\text{EQE}}$, as a function of the wavelength, for BEDOT-BBT:C$_{60}$ bilayer cell. Inset: the schematic energy level diagram of this cell.

The EQE of BEDOT-BBT based cells is higher than the BEDOT-TQMe$_2$, achieving 1.5\% at the maximum peak but still at very low level, as shown in Figure 7-4. Except for the contribution from C$_{60}$ at peaks of 350 nm and 440 nm, we can clearly find the BEDOT-BBT peak at about 650 nm (Figure 4-2) with peak value of 0.7\%.

The above preliminary results of OPV devices based on the two DAD oligomers indicate that the molecular structures of DAD oligomers need to be carefully designed to have certain properties such as high conductivity, high absorption coefficient, appropriate energy band gaps and HOMO/LUMO levels, for the application of high efficiency OPV devices. And those properties can be easily tuned by connecting different donor and acceptor units for the DAD oligomers.

Furthermore, the highly phosphorescence Pt-porphyrins in this dissertation can be dissolved in solvent or be thermal evaporated, so both vapor thermal evaporation and solution processing methods can be used for OPV device fabrication. The conductivity
might be an issue before applying to the OPV devices. The cost will be another concern since some of the phosphorescent near-IR emitters contain the expensive heavy metals.

### 7.2.3 Ultra-Violet OLEDs of Shorter Emission

We already realize the importance of appropriate energy level alignment for the multilayer devices, in order to extract the desiring light emission from the UV emitters. In Chapter 6, we already successfully achieve the violet-UV emitting OLEDs with peak emission wavelength below 400 nm, at $\lambda = 393$ nm. However, UV emitting OLEDs with even shorter emission wavelengths are still needed.

![Absorption (dashed red line) and PL spectra of t-BuBP4M in the solution (dashed blue line) and solid-state film (solid blue line) when excited at $\lambda_{ex} = 270$. Inset: molecular structure of UV emitting t-BuBP4M.](image)

Based on a new UV emitter, t-BuBP4M, with PL emission peak wavelength at $\sim332$ nm in the solution, as shown in Figure 7-5, we have tried to fabricate the UV emitting OLEDs. The PL emission measured in solid state film is also shown in Figure 7-5, in which $\sim30$ nm red shift of PL emission peaks is observed, indicating that the t-BuBP4M have very strong inter-molecular interaction. So the t-BuBP4M needs to be dispersed into host matrix to avoid the aggregate-induced red-shifted emission.
Figure 7-6. (color) Normalized EL spectra for the OLEDs with t-BuBP4M doped in UGH2 host matrix with different doping concentrations (1%, 5% and 10%). TAPC and BCP are used as the HTL and ETL, respectively, for these devices.

We first use very wide band gap UGH2 (~4.4 eV) as the host matrix doped with t-BuBP4M of different doping concentrations. TAPC and BCP are used as the HTL and ETL, respectively, in these devices. As shown in Figure 7-6, all the devices show no UV emission as indicated by the PL spectra of t-BuBP4M (Figure 7-5). The longer emissions peaked at approximately 450 nm and 650 nm are probably due to the exciplex emission at the interfaces.

OLEDs with other device structures are then fabricated as shown in Figure 7-7, to better align the energy levels of different layers.\textsuperscript{106,108} However, none of these devices shows the similar emission as the solution PL spectra or even the solid-state film PL spectra of t-BuBP4M. For example, the neat t-BuBP4M film is used as the EML layer with TcTa and TPBi as the HTL and ETL, respectively. The device only shows a noisy and unstable peak at wavelength of ~380 nm. The host material used in previous purine based devies, mCP, also does not work for the t-BuBP4M based devices. The insertion
of thin buffer layer of UGH2 between the host and ETL layers does not help, either. These devices show no UV emission from t-BuBP4M and similar to the EL spectrum of control device with only neat mCP layer sandwiched by TcTa and TPBi layers.

![Normalized EL spectra for the OLEDs based on t-BuBP4M (UV) with different device structures](image)

Figure 7-7. (color) Normalized EL spectra for the OLEDs based on t-BuBP4M (UV) with different device structures.

The existing organic materials used in OLEDs are mostly for the application of visible light emitting OLEDs, in which charges can be easily injected and then effectively confined, and energy transfer can successfully occur. But for UV OLEDs, as mentioned in the above of the t-BuBP4M based devices, it is not the case. Due to the wide band gap of the UV emitters ($E_g > 3.3$ eV), the host materials should have even wider gap than UV emitters, so that the energy transfer effectively occurs. The HTL layers should have shallower LUMO levels to effectively confine the injected electrons. The HOMO levels of HTL also need to be deeper, to reduce the injection barrier of holes from anode. A hole injection layer (HIL) may also help. Similar requirement including effectively
injecting electrons and confining holes also apply to the ETL layer. At the same time, the emission of exciplex occurred at the interface of organic layers also need to be eliminated by changing the interface properties or energy level alignment.

So, the materials of HTL, host and ETL need to be carefully designed and synthesized specifically for UV OLEDs fabrication. However, even the energy level alignment is finally achieved; there are still lots of other issues that will affect the device performance such as the device stability and efficiency. So it is still very challenging but promising to achieve the OLEDs emitting UV light in the future.
APPENDIX A
LIST OF ORGANIC MOLECULAR STRUCTURES

This table lists the molecular structures for all the organic materials used in this dissertation. Please refer to LIST OF ABBREVIATIONS for full name of each molecule.

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<td><img src="image8" alt="3TPYMB structure" /></td>
</tr>
</tbody>
</table>
APPENDIX B
LIST OF PUBLICATIONS AND CONFERENCES


LIST OF REFERENCES


117 J. D. Wright, Molecular Crystals, 2nd ed. (Cambridge University Press, 1995).


BIOGRAPHICAL SKETCH

Yixing Yang was born in Jinhua, China in 1985. He grew up in the same city with good academic education, and finished his middle school there in 2000, with top 3 ranking in the whole school. Then he graduated from Jinhua No.1 High School in 2003. In the same year he was admitted to one of the best colleges in China, University of Science and Technology of China (USTC), for higher level education.

In 2007, he successfully graduated from USTC with a bachelor’s degree of Polymer Science and Engineering. Because of the outstanding academic performance there, he was honored with the Presidential Guo Moruo Scholarship. At fall of 2007, he traveled abroad to United States and started to pursue his Doctorate degree in the Department of Materials Science and Engineering at University of Florida. Working on the research fields of organic light emitting devices and organic photovoltaic devices, he became a well-qualified and dedicated researcher in organic semiconductor thin film deposition, device fabrication and characterization. He published more than 10 peer-reviewed papers in scientific journals and attended several international conferences. Under the supervision of his advisor, Dr. Jiangeng Xue, in December 2011, he received his Doctor of Philosophy degree in the Department of Materials Science and Engineering at University of Florida.